

PATENT ABSTRACTS OF JAPAN

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(54) ZIRCONIUM-CERIUM-BASED COMPOUND OXIDE AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a zirconium-cerium-based compound oxide excellent in heat resistance, capable of maintaining a high specific surface area even in the case of use in a high-temperature environment and to provide a method capable of producing the compound oxide in excellent reproducibility and economically.

SOLUTION: This zirconium-cerium-based compound oxide is a compound oxide baked at 500-1,000°C, comprises zirconium and cerium, has the blending ratio of zirconium and cerium calculated as zirconium oxide and ceric oxide of (51-95):(45-5) by weight, shows at least 50m²/g specific surface area after baking at 500-1,000°C, maintains at least 20m²/g specific surface area after heating at 1,100°C for 6 hours and contains 0.1-20wt.% of the total calculated as oxide of at least one selected from the group consisting of yttrium, scandium, lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, magnesium, calcium, barium, aluminum, titanium and hafnium.

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CLAIMS

[Claim(s)]

[Claim 1] It is the multiple oxide calcinated and obtained at 500-1000 degrees C. This multiple oxide The rate of a compounding ratio of said zirconium converted into a zirconium dioxide and the second cerium of oxidization and a cerium including a zirconium and a cerium Are 51-95:49-5 in a weight ratio, and the specific surface area after calcinating at said 500-1000 degrees C shows at least 50m²/g. And the zirconium-cerium system multiple oxide characterized by maintaining the specific surface area of at least 20m²/g after 6-hour heating at 1100 degrees C.

[Claim 2] The zirconium-cerium system multiple oxide according to claim 1 characterized by containing one sort chosen from the group which said multiple oxide becomes from an yttrium, a scandium, a lanthanum, a praseodymium, neodymium, samarium, europium, a gadolinium, magnesium, calcium, barium, aluminum, titanium, and a hafnium further, or two sorts or more 0.1 to 20% of the weight with the total quantity which carries out oxide conversion.

[Claim 3] The manufacture approach of the zirconium-cerium system multiple oxide according to claim 1 or 2 which is made to carry out the pyrogenetic reaction of the mixture containing zirconium hydroxide of 0.5-50 micrometers of mean diameters, and the cerium sol of 3-100nm of mean diameters of a colloidal particle to the number of cerium mols in this mixture to the bottom of the nitric-acid existence of a five to 10 time mol, adds a base, is subsequently made to react further, calcinates the obtained product at 500-1000 degrees C, and is characterized by grinding.

[Claim 4] The manufacture approach of the zirconium-cerium system multiple oxide containing one sort chosen from the group which said mixture becomes from the salts of an yttrium, a scandium, a lanthanum, a praseodymium, neodymium, samarium, europium, a gadolinium, magnesium, calcium, barium, aluminum, titanium, and a hafnium, or two sorts or more according to claim 3.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is available in the catalyst field, the functional-ceramics field, the solid electrolyte field for fuel cells, etc., and relates to the zirconium-cerium system multiple oxide which has the available outstanding thermal resistance suitably especially as a co-catalyst ingredient in the catalyst for emission gas purification of an automobile, and its manufacturing method.

[0002]

[Description of the Prior Art] The co-catalyst for raising the platinum which is a catalyst metal, palladium, rhodiums, etc. and these catalyses to catalyst support, such as an alumina and cordierite, is supported, and catalysts for emission gas purification, such as an automobile, are constituted. The cerium oxide system ingredient as this co-catalyst ingredient absorbs oxygen under an oxidizing atmosphere, and in order to purify at the effectiveness which was excellent with the property of the cerium oxide of emitting that oxygen under reducing atmosphere, and the so-called oxygen uptake and emission ability, in a hydrocarbon, a carbon monoxide, nitrogen oxides, etc. which are the injurious ingredients in exhaust gas, it is used in large quantities. Moreover, since a zirconium dioxide raises the property of said cerium oxide, as a co-catalyst ingredient, a zirconium-cerium system multiple oxide becomes in use, and the rate of an use rate has been increasing it.

[0003] When operating the co-catalyst ingredient of this system, the most important thing is maintaining an elevated temperature, and like [at the time of engine starting], when the temperature of exhaust gas is low, purification effectiveness is bad. In recent years, an automaker is going to bring the distance of an engine and catalyst equipment close, and it is going to cope with this problem by introducing the elevated-temperature exhaust gas immediately after exhaust air into catalyst equipment.

[0004] However, a new problem arose about the thermal resistance of a catalyst ingredient in this case. The specific surface area of the co-catalyst ingredient used from generally the effectiveness of the offgas treatment by the catalyst being proportional to the activity phase of a catalyst and the touch area of exhaust gas must be fully large. However, the co-catalyst ingredient with which the particle of the present zirconium-cerium system multiple oxide cannot be said to be enough about thermal resistance, but is stabilized since specific surface area falls with grain growth in the operating environment of elevated-temperature long duration, and high specific surface area is maintained is called for strongly.

[0005] About the manufacture approach of a zirconium-cerium system multiple oxide excellent in the conventional thermal resistance, the method of mixing a zirconium sol and a cerium sol to JP,6-279027,A and JP,8-16015,B, and adding a base, for example to them or the approach using spray drying is proposed. And about the thermal resistance of the obtained mixed oxide, it is indicated that the specific surface area after 1000-degree-C temporary quenching is 15m²/g. The manufacture approach of a mixed oxide of calcinating the mixture of the hydration zirconia sol of 0.2 micrometers or less of mean diameters and compounds, such as Ce, Y, calcium, and Mg, is proposed by JP,5-193948,A, and, as for the thermal resistance of the obtained mixed oxide, it is indicated that the specific surface area after 1050-degree-C temporary quenching is 12m²/g. The manufacture approach of a mixed oxide of calcinating the mixture of the hydration zirconia sol of 0.05-0.3 micrometers of mean diameters and 4nm or less of diameters of microcrystal and compounds, such as Ce, Y, calcium, and Mg, is proposed by JP,5-116945,A, and, as for the thermal resistance of the obtained mixed oxide, it is indicated that the specific surface area after 850-degree-C baking is 15m²/g. Moreover, as the manufacture approach of a zirconic acid ghost, the approach which mixes the hydroxide, hydration oxide, oxide, etc. of the metal more than divalent in a zirconium salt water solution, and it is made to hydrolyze is proposed by JP,5-155622,A, and, as for the thermal resistance of the obtained mixed oxide, it is indicated that the specific surface area after 1000-degree-C baking is 8m²/g.

[0006] Any above approach has the problem that the operate time which manufactures the target oxide is long. For example, by the approach [need / a zirconia sol / to be received], a problem is in productivity, like the hydrolysis time amount of a zirconium salt water solution exceeds 100 hours.

[0007] Moreover, as an approach of only obtaining high specific surface area, the manufacture approach using the zirconia sol (5-500nm detailed zirconia colloidal particle) indicated by JP,6-279027,A and JP,8-16015,B is [that what is necessary is just to control, the diameter of microcrystal i.e., the crystal growth degree, of an oxide,] the optimal. However, although the crystal and particle diameter in the condition of an oxide are detailed therefore, to heat energy, it is very sensitive, and in sintering by the pyrosphere 900 degrees C or more, specific surface area becomes small remarkably and the oxide obtained by the manufacture approach of these known has the problem that thermal resistance is bad. That is, it is not suitable for the co-catalyst ingredient by which elevated-temperature use is carried out. Furthermore, by many manufacture approaches by which the conventional proposal is made, there is also a problem that impurity mixing of chlorine harmful for the catalyst resulting from a raw material, sulfur, etc. is not avoided.

[0008]

[Problem(s) to be Solved by the Invention] Therefore, especially the purpose of this invention is to offer the zirconium-cerium system multiple oxide which can maintain a high specific surface area, and its manufacture approach, when it has the thermal resistance which was excellent as a co-catalyst ingredient suitable for the catalyst for emission gas purification and is used under hot environments. Another purpose of this invention is to offer the manufacture approach which can prepare often [repeatability] and economically the zirconium-cerium system multiple oxide which has the outstanding thermal resistance. Other purposes of this invention are to offer the manufacture approach of a zirconium-cerium system multiple oxide without mixing of impurities, such as chlorine harmful for a catalyst, and sulfur, while having the outstanding thermal resistance.

[0009]

[Means for Solving the Problem] When the zirconium-cerium system multiple oxide by the conventional technique had a big specific surface area and this invention person heated to the elevated temperature, he did detailed research about the effect of a zirconium raw material about the cause that specific surface area falls rapidly. Consequently, the water solution of the zirconium sol known as an

approach of obtaining the high multiple oxide of whenever [dissolution-with zirconium dioxide and cerium oxide] conventionally, or a zirconium salt, The multiple oxide precursor which the cerium sol or the cerium salt water solution was mixed [precursor], and made the base add and generate Probably because it was microcrystal nature, although it is very sensitive and the zirconium-cerium system multiple oxide which has the crystal phase of the high single phase of whenever [dissolution] by baking was generated to heat energy, the fall of the specific surface area by sintering by the pyrosphere was remarkable, and checked that high specific surface area was unmaintainable. Then, when a trial-and-error method was applied to the attempt which raises crystallinity in the phase of a precursor, as a result of considering the use and the effect of grain size of the zirconium hydroxide particle which was not taken up until now as a zirconium raw material in such a multiple oxide application of high specific surface area, the reaction approach for obtaining the precursor which compounded the cerium component or the addition component of further others is developed by using this particle as a parent, and it came to complete this invention.

[0010] Namely, according to this invention, it is the multiple oxide calcinated and obtained at 500-1000 degrees C. The rate of a compounding ratio of said zirconium which this multiple oxide converted into a zirconium dioxide and the second cerium of oxidization including the zirconium and the cerium, and a cerium is 51-95:49-5 in a weight ratio. As occasion demands Furthermore, an yttrium, a scandium, a lanthanum, a praseodymium, neodymium, Samarium, europium, a gadolinium, magnesium, calcium, One sort chosen from the group which consists of barium, aluminum, titanium, and a hafnium, or two sorts or more The specific surface area after containing 0.1 to 20% of the weight with the total quantity which carries out oxide conversion and calcinating at said 500-1000 degrees C shows at least 50m²/g. And the zirconium-cerium system multiple oxide characterized by maintaining the specific surface area of at least 20m²/g after 6-hour heating at 1100 degrees C is offered. According to this invention, moreover, zirconium hydroxide of 0.5-50 micrometers of mean diameters, The need is accepted again in a cerium sol with a mean particle diameter [of a colloidal particle] of 3-100nm. An yttrium, A scandium, a lanthanum, a praseodymium, neodymium, samarium, europium, A gadolinium, magnesium, calcium, barium, aluminum, The pyrogenetic reaction of the mixture containing one sort chosen from the group which consists of salts of titanium and a hafnium, or two sorts or more is carried out to the number of cerium mols in this mixture to the bottom of the nitric-acid existence of a five to 10 time mol. Subsequently Add a base, it is made to react further and the manufacture approach of said zirconium-cerium system multiple oxide characterized by calcinating and grinding the obtained product at 500-1000 degrees C is offered.

[0011]

[Embodiment of the Invention] It is [following] this invention, and also explains to a detail. In the zirconium-cerium system multiple oxide of this invention, as for a multiple oxide, a zirconium dioxide and cerium oxide only say not a condition but the thing which forms a multiple oxide thru/or the solid solution partially or substantially of mixture. Although a cerium oxide component shows oxygen uptake and emission ability when this multiple oxide is used as a co-catalyst ingredient, a zirconium dioxide component raises the thermal resistance of this cerium oxide, and has the operation which demonstrates oxygen uptake and emission ability in a large temperature requirement.

[0012] the weight ratio which converted the rate of a compounding ratio of the zirconium to contain and a cerium into a zirconium dioxide (ZrO₂) and the second cerium (CeO₂) of oxidation in the multiple oxide of this invention -- 51-95:49-5 -- desirable -- 55-85:45-15 -- it is 60-80:40-20 still more preferably. If the thermal resistance the rate of a compounding ratio of a zirconium dioxide excelled [thermal resistance] less than in 51 is not fully obtained and 95 is exceeded, the oxygen uptake and emission ability by the cerium oxide component run short. The sum total content rate of the zirconium in a multiple oxide and a cerium has 80 desirable % of the weight or more at a zirconium dioxide and the second cerium conversion of oxidation.

[0013] The specific surface area after calcinating and obtaining the multiple oxide of this invention at 500-1000 degrees C and calcinating in this temperature requirement shows at least 50m²/g, and specific surface area usually becomes low, so that burning temperature is high. For example, more than 70m²/g, if it is baking of 6 hours at 500 degrees C and is baking of 6 hours at 900 degrees C more than 90m²/g, if it is baking of 6 hours at 1000 degrees C, a high specific surface area more than 50m²/g is shown. The ingredient which has the specific surface area of the high level in such a burning temperature is not conventionally known as a zirconium-cerium system multiple oxide. And the multiple oxide of this invention has the engine performance which maintains the specific surface area of at least 20m²/g after 6-hour heating at 1100 degrees C. When heating oxide powder generally, sintering and grain growth become remarkable more than the temperature field of the specification depending on a presentation and the manufacture hysteresis of the powder, and the rapid fall of specific surface area arises. It is known for 1000 degrees C or more of profiles in a zirconium-cerium system multiple oxide that this reduction is remarkable, and it is designed so that the present catalyst equipment for emission gas purification may also usually work below about 900 degrees C. In order for the elevated temperature around 1000 degrees C called for in this invention from now on to show the engine performance of an usable multiple oxide to an usable co-catalyst ingredient etc., the value of the specific surface area currently maintained after 6-hour heating at 1100 degrees C on the basis of 1100 degrees C it is considered that is the upper limit of the temperature used as heat-resistant evaluation temperature of the obtained multiple oxide was made into the engine-performance index of a multiple oxide. In addition, in this invention, specific surface area is the value measured based on the BET adsorption method by the most standard nitrogen gas adsorption as a specific-surface-area measuring method of fine particles.

[0014] The multiple oxide of this invention may carry out the oxide conversion of one sort chosen from the group which consists of an yttrium, a scandium, a lanthanum, a praseodymium, neodymium, samarium, europium, a gadolinium, magnesium, calcium, barium, aluminum, titanium, and a hafnium further, or the two sorts or more besides a zirconium and a cerium, and may contain them in 0.1 - 20% of the weight of the range with the total quantity. By making such a specific metal contain further, it is possible to give the further excellent thermal resistance. Under the present circumstances, at less than 0.1 % of the weight, since the oxygen uptake and emission ability demanded when the content of a cerium falls relatively and uses it for a co-catalyst etc. run short if effectiveness is not accepted in a heat-resistant improvement and 20 % of the weight is exceeded, it is not desirable.

[0015] The manufacture approach of this invention can prepare said multiple oxide often [repeatability] and economically. By this manufacture approach, the pyrogenetic reaction of the mixture containing a specific zirconium raw material and a specific specific cerium raw material is first carried out to the bottom of the nitric-acid existence of the amount of specification.

[0016] 1-30 micrometers of said specific zirconium raw materials are 5-25-micrometer zirconium hydroxide still more preferably preferably the mean particle diameter of 0.5-50 micrometers. When mean particle diameter is less than 0.5 micrometers, the multiple oxide of high specific surface area excellent in the thermal resistance made into the purpose of this invention is not obtained, but when exceeding 50 micrometers, the specific surface area of a multiple oxide falls. This zirconium hydroxide is the generic name of (1) zirconium-hydroxide Zr(OH)₄ and nH₂O, (2) oxy-zirconium hydroxide ZrO(OH)₂ and nH₂O, and (3) hydration zirconia ZrO₂ and nH₂O, and it can use as independent or mixture. Although said zirconium hydroxide can usually come to hand from a commercial item in the state of fine particles, it can be obtained by well-known approaches, such as adding bases, such as aqueous ammonia, ammonia gas, a sodium hydroxide, and a potassium hydroxide, for example to zirconium salt water solutions, such as a zirconium

nitrate, a zirconium chloride, and zirconium nitrate. It is advantageous at the point that the process of a zirconium nitrate-ammonia system does not contain harmful impurities, such as chlorine and sulfur, especially. In addition, the grading-analysis meter (MKII mold) by the Leeds & North lap company based on a laser diffraction method performed measurement of mean particle diameter. [0017] 5-80nm of said specific cerium raw materials is a 10-50nm cerium sol still more preferably preferably the mean particle diameter of 3-100nm of a colloidal particle. This cerium sol means the thing in the condition that the cerium oxide of colloidal particle size, hydration cerium oxide, the hydroxylation cerium, or the solid-state particle (colloidal particle) of two or more forms distributed in the aqueous medium so that I may generally be understood. Industrially [when the mean particle diameter of a colloidal particle is less than 3nm], manufacture is difficult, and when exceeding 100nm, in a back process, compound-ization with a zirconium dioxide cannot advance easily. In addition, the dynamic light scattering photometer (DLS-7000 mold) by the Otsuka electronic company based on a dynamic-light-scattering measuring method performed measurement of the diameter of a colloidal particle. Especially the manufacturing method of said cerium sol is not limited, and is acquired by the well-known method of making the second cerium water solution of a nitric acid hydrolyze etc., and can use a thing with a concentration of about 100-200g /l.] by cerium oxide conversion as a commercial item. In order to hold a sol condition to stability, its either is usable although a commercial cerium sol has nitric-acid acidity or the thing by which acetic-acid acidity is carried out. However, use of few [as much as possible] things of a residual of impurities, such as chlorine resulting from the raw material when manufacturing a cerium sol and sulfur, is desirable.

[0018] As for the mixed rate of said zirconium hydroxide and said cerium sol, in said mixture, it is desirable to mix so that the mixed rate which could set up suitably so that it might become a theoretical ratio corresponding to the presentation ratio of a desired zirconium-cerium system multiple oxide, for example, converted the zirconium and the cerium into a zirconium dioxide and the second cerium of oxidation may be set to 51-95:49-5 by the weight ratio. As for preparation of mixture, it is desirable to carry out weighing capacity of said zirconium hydroxide and said cerium sol, to mix with the water of optimum dose and to consider as slurry-like mixture. Said zirconium hydroxide in mixture and especially the concentration of said cerium sol have l. desirable at the total quantity of oxide conversion in 20-150g /l. 10-200g /. One sort chosen as said mixture from the group which consists of salts of an yttrium, a scandium, a lanthanum, a praseodymium, neodymium, samarium, europium, a gadolinium, magnesium, calcium, barium, aluminum, titanium, and a hafnium further if needed, or two sorts or more can be added. As salts, although it can choose from a nitrate, a chloride, a sulfate, and other water-soluble salts, if it is the compound dissolved and ionized when it heats under nitric-acid acidity in degree process also except a water-soluble salt, it is usable. The nitrate which does not remain in the multiple oxide with which especially a harmful impurity is obtained is desirable. As for the amount of mixing of these salts, it is desirable to carry out weighing capacity and to mix in the multiple oxide obtained, by theoretical ratio from which the total quantity which carries out oxide conversion becomes 0.1 - 20 % of the weight. Detailed distribution of the mixed components other than these zirconiums and a cerium is carried out as dissolution thru/or an oxide into the multiple oxide obtained, and it has the operation which bars the crystal growth of the multiple oxide in an elevated temperature.

[0019] performing the pyrogenetic reaction of said mixture under churning -- desirable -- this time -- the number of cerium mols in mixture -- receiving -- a five to 10 time mol -- desirable -- a 5.5 to 8 time mol -- it is necessary to make the nitric acid of a mol exist 5.8 to 7 times still more preferably What is necessary is for it to be total, and just to add a nitric acid by the thing of the type stabilized with acetic-acid acidity also including the amount of nitric acids, that what is necessary is just to prepare so that a nitric acid may serve as the above-mentioned number of mols so that it may become the above-mentioned number of mols when the thing of the type stabilized with nitric-acid acidity as the above-mentioned cerium sol is used. By making the nitric acid of such an amount of specification exist, the crystal of each particle of zirconium hydroxide and a cerium sol repeats elution and a deposit, and crystal growth can be advanced, performing compound-ization of a zirconium and a cerium. A nitric acid cannot give the thermal resistance excellent in the multiple oxide which can become inadequate [crystal growth] under by the 5 time mol. On the other hand, since a zirconium hydroxide particle will dissolve and the zirconium of an ionic state will increase if a mol is exceeded 10 times, the precursor which detailed precipitate produces in a reaction with the base mentioned later, and this invention means and which fully grew is not obtained, and the multiple oxide excellent in thermal resistance is not obtained.

[0020] The reaction temperature of 60-150 degrees C, preferably, the pyrogenetic reaction under said nitric-acid existence is 80-140 degrees C, and can be performed in reaction-time 1 - 36 hours. It can carry out under ordinary pressure or pressurization preferably. When carrying out under pressurization, it is possible to shorten reaction time by carrying out under about 1.5-10kg/cm2 pressurization using pressurization containers, such as an autoclave.

[0021] Subsequently a base is added and it is made to react further by the manufacture approach of this invention. After cooling especially preferably 60 degrees C or less of mixture made to react under existence of said nitric acid at 50 degrees C or less in this reaction, for example, a base can be added, churning etc. can be carried out and a reaction can be advanced. As a base, although a sodium hydroxide, a potassium hydroxide, aqueous ammonia, ammonia gas, or such mixture can be mentioned, it is aqueous ammonia preferably. Addition of a base uses a base as the water solution of moderate concentration, and in the case of the approach of adding, while agitating into said cooled mixture, and ammonia gas, it can carry out by the approach of blowing into a container etc., agitating. If it is judged easily and pH exceeds 10 by following change of pH of mixture, the limit of the amount of the base to add will be enough and a reaction will complete it. The solid and metal ion which existed in mixture are substantially compound-ized altogether by this reaction, and can settle the product to which crystal growth progressed by it. Drawing 1 and drawing 2 are the results of carrying out X diffraction measurement of the product of this phase in the example (example 1) and the example 1 of a comparison of this invention which are mentioned later on the same conditions (the term of an example describing), and it turns out that the crystallinity of the product by this invention is high. It becomes a suitable precursor in order that this product may obtain the multiple oxide of the request excellent in thermal resistance. This precursor is separable by for example, the nutsche method, the centrifuge method, the filter press method, etc. Moreover, rinsing of precipitate can also be added to need extent. Furthermore, in order to raise the effectiveness of the following baking process, the process which dries the obtained precipitate moderately may be added.

[0022] By the manufacture approach of this invention, a desired multiple oxide can be obtained by calcinating and grinding said obtained product at specific temperature. Burning temperature can choose the temperature of the arbitration between 500-1000 degrees C. Having made minimum temperature into 500 degrees C is based on the following reason. In drawing 3, the result of having measured heating weight change of a product using the thermobalance (Rigaku electrical machinery company manufacture TG-DTA-812H mold use) shows having completed weight reduction at 500 degrees C. That is, at less than 500 degrees C, a zirconium-cerium system multiple oxide has an incomplete burning temperature, and since the hydroxyl group, the acid radical, the base, etc. remain, in case it is used under an elevated temperature, since they are emitted, it cannot adopt. Drawing 4 compares and investigates change of the diameter of microcrystal to burning temperature (6 hours each) in a temperature field 500 degrees C or more about the multiple oxide by this invention (the below-mentioned example 1) and the example 1 of a comparison. Drawing 5 is change of the specific surface area corresponding to them. Both drawings show maintaining a high specific surface area that it is [therefore] hard to make microcrystal big and rough (a degree of sintering is), even when the multiple oxide by this invention calcinates by the pyrosphere.

Although the burning temperature for considering as a desired multiple oxide can be chosen as arbitration from the specific surface area which it is required or is guaranteed, and the value of bulk density, an upper limit is limited to 1000 degrees C or less from a practical viewpoint as a co-catalyst ingredient of thinking specific surface area as important. 500-800 degrees C is 500-600 degrees C still more preferably. On balance with temperature, firing time may be set up suitably and is 1 - 10 hours preferably. If the range of the multiple oxide by this invention is 500-1000 degrees C -- the baking condition -- it is not based on how, but has the outstanding thermal resistance, and, in addition, has a high specific surface area more than 20m²/g in heating for 1100-degree-C 6 hours.

[0023] Said grinding can carry out the calcinated multiple oxide using the grinder generally used, for example, a hammer mill etc., and can obtain the powder of a desired grain size enough. Since this has the small degree of sintering of the obtained multiple oxide, a grindability is good and is based on things.

[0024]

[Effect of the Invention] Since the multiple oxide of this invention uses the multiple oxide of a zirconium and a cerium as a principal component, it has a high specific surface area and it has the outstanding thermal resistance which maintains the specific surface area of at least 20m²/g after 1100-degree-C heating of 6 hours especially. It especially replaces with the conventional zirconium-cerium system multiple oxide, and can use as a co-catalyst of the catalyst for emission gas purification etc., use by the pyrosphere beyond the conventional limitation is possible, and it is very useful in the field of the efficient catalyst for emission gas purification. Moreover, in the manufacturing method of this invention, the multiple oxide which has said high specific surface area and high thermal resistance can be obtained often [repeatability] and economically.

[0025]

[Example] Hereafter, although an example and the example of a comparison explain to a detail further, this invention is not limited to these.

[0026] 81.05g (triple-purpose metal industrial stock type firm make, 99.9% of purity, the zirconium dioxide conversion content of 40.1 % of the weight, mean particle diameter of 18.56 micrometers) of example 1 zirconium hydroxide, Cerium sol (Rhone-Poulenc S.A. make, cerium ion content [of 5 or less % of the weight], cerium oxide conversion concentration of 100g/l.) 150ml, 16.67ml (Anan formation incorporated company make, purity of 99.9%, lanthanum trioxide conversion concentration of 150g/l.) of lanthanum nitrate water solutions was mixed, and the mixture of ZrO₂:CeO₂:La₂O₃=65:30:5 (weight ratio) was obtained. Into the obtained mixture, further, it added so that it might exist by the mol 6 times, and 1l. of total cerium mol mixture adjusted by desalted water so that oxide conversion concentration might become in 1. and 50g /further was obtained for the nitric acid (the Wako Pure Chem Industries make, 60 - 61% of purity). Subsequently, 1l. of obtained mixture was moved to the container equipped with the steam cooling pipe (capacitor), and it heated under churning at 100 degrees C for 12 hours. After cooling slowly to 20 degrees C, it added under churning of aqueous ammonia (the Wako Pure Chem Industries make, 25 - 28 % of the weight of NH₃ contents), and pH was adjusted to ten or more. Solid liquid separation was performed for the obtained product by the nutsche, and 139.23g of precipitate was obtained. The obtained precipitate was measured with the Rigaku X-ray diffractometer "RINT1100 mold" by CuK alpha rays, the tube voltage of 40kV, and 40mA of tube electric currents. An X diffraction image is shown in drawing 1 . Although the exact diameter of microcrystal cannot be measured, the X-ray intensity which shows crystallinity was about 700cps. Obtained sediment was calcinated at 500 degrees C for 6 hours, and 50g of zirconium-cerium system lanthanum content multiple oxides of specific-surface-area of 92.7m²/g was obtained. The specific surface area when heating the obtained multiple oxide for 6 hours each at 900 more degrees C, 1000 degrees C, and 1100 degrees C is shown in Table 1 and drawing 5 . Moreover, the diameter of microcrystal for which it asked from the X diffraction image is shown in drawing 4 . The specific surface area after 6-hour heating was 24.7m²/g at 1100 degrees C. As a result of the component analysis, the zirconium in a multiple oxide, the cerium, and the content rate of a lanthanum were a zirconium dioxide, the second cerium of oxidation, and lanthanum trioxide conversion, and were 65.1 % of the weight, 29.9 % of the weight, and 5 % of the weight, respectively.

[0027] 93.52g of zirconium hydroxide, cerium sol 100ml, and 16.67ml of lanthanum nitrate water solutions used in the example 2 example 1 were mixed, and the mixture of ZrO₂:CeO₂:La₂O₃=75:20:5 (weight ratio) was obtained. Into the obtained mixture, further, it added so that it might exist by the mol 6.2 times, and 1l. of total cerium mol mixture adjusted by desalted water so that oxide conversion concentration might become in 1. and 50g /further was obtained for the nitric acid. Subsequently, it agitated and heated like the example 1, aqueous ammonia was added, solid liquid separation of a product was performed, and 142g precipitate was obtained. X diffraction measurement of the obtained precipitate was carried out on an example 1 and these conditions. Although the exact diameter of microcrystal cannot be measured, the X-ray intensity which shows crystallinity was about 700cps. Furthermore, it calcinated like the example 1 and 50g of zirconium-cerium system lanthanum content multiple oxides of specific-surface-area of 115.7m²/g was obtained. The specific surface area when heating the obtained multiple oxide for 6 hours each at 900 more degrees C, 1000 degrees C, and 1100 degrees C is shown in Table 1. Made in [after 6 hour heating] the non-front face was 22.4m²/g at 1100 degrees C. As a result of the component analysis, the zirconium in a multiple oxide, the cerium, and the content rate of a lanthanum were a zirconium dioxide, the second cerium of oxidation, and lanthanum trioxide conversion, and were 74.9 % of the weight, 20.2 % of the weight, and 4.9 % of the weight, respectively.

[0028] 93.52g of zirconium hydroxide used in the example 3 example 1 and cerium sol 125ml were mixed, and the mixture of ZrO₂:CeO₂= 75:25 (weight ratio) was obtained. Into the obtained mixture, further, it added so that it might exist by the mol 5.5 times, and 1l. of total cerium mol mixture adjusted by desalted water so that it might become the oxide conversion concentration of 50g/l. further was obtained for the nitric acid. Subsequently, it carried out like the example 1 and 141.62g precipitate was obtained. X diffraction measurement of the obtained precipitate was carried out on an example 1 and these conditions. Although the exact diameter of microcrystal was not able to be measured, the X-ray intensity which shows crystallinity was about 700cps. Furthermore, it carried out like the example 1 and 50g of zirconium-cerium multiple oxides of specific-surface-area of 112.4m²/g was obtained. The specific surface area when heating the obtained multiple oxide for 6 hours each at 900 more degrees C, 1000 degrees C, and 1100 degrees C is shown in Table 1. Made in [after 6 hour heating] the non-front face was 20.4m²/g at 1100 degrees C. Moreover, as a result of the component analysis, the zirconium in a multiple oxide and the content rate of a cerium were a zirconium dioxide and the second cerium conversion of oxidation, and were 75 % of the weight and 25 % of the weight, respectively.

[0029] 16.67ml (Anan formation incorporated company make, purity of 99.9%, neodymium oxide conversion concentration of 150g/l.) of nitric-acid neodymium water solutions was mixed with 81.05g of zirconium hydroxide used in the example 4 example 1, and cerium sol 150ml, and the mixture of ZrO₂:CeO₂:Nd₂O₃=65:30:5 (weight ratio) was obtained. Furthermore, it added so that it might exist by the mol 6.5 times, and 1l. of total cerium mol mixture adjusted by desalted water so that it might become the oxide conversion concentration of 50g/l. further was obtained for the nitric acid. Subsequently, it carried out like the example 1 and 138.24g precipitate was obtained. X diffraction measurement of the obtained precipitate was carried out on an example 1 and these conditions. Although the exact diameter of microcrystal was not able to be measured, the X-ray intensity which shows crystallinity was about

700cps. It carried out still like the example 1 and 50g of zirconium-cerium system neodymium content multiple oxides of specific-surface-area of 91.3m²/g was obtained. The specific surface area when heating the obtained multiple oxide for 6 hours each at 900 more degrees C, 1000 degrees C, and 1100 degrees C is shown in Table 1. The specific surface area after 6-hour heating was 23.8m²/g at 1100 degrees C. As a result of the component analysis, the content rates of the zirconium in a multiple oxide, a cerium, and neodymium were a zirconium dioxide, the second cerium of oxidation, and neodymium oxide conversion, and were 65 % of the weight, 30.1 % of the weight, and 4.9 % of the weight, respectively.

[0030] 16.67ml (water solution of an aluminium nitrate and 9 hydrate by Wako Pure Chem Industries, 99.9% of purity, and aluminum-oxide conversion concentration 150 g/l) of aluminium nitrate water solutions was mixed with 81.05g of zirconium hydroxide used in the example 5 example 1, and cerium sol 150ml, and the mixture of ZrO₂:CeO₂:aluminum₂O₃=65:30:5 (weight ratio) was obtained. Furthermore, it added so that it might exist by the mol 6.1 times, and 1l. of total cerium mol mixture adjusted by desalted water so that it might become the oxide conversion concentration of 50g/l. further was obtained for the nitric acid. Subsequently, it carried out like the example 1 and 137.94g precipitate was obtained. X diffraction measurement of the obtained precipitate was carried out on an example 1 and these conditions. Although the exact diameter of microcrystal was not able to be measured, the X-ray intensity which shows crystallinity was about 700cps. It carried out still like the example 1 and 50g of zirconium-cerium system aluminum content multiple oxides of specific-surface-area of 90.9m²/g was obtained. The specific surface area when heating the obtained multiple oxide for 6 hours each at 900 more degrees C, 1000 degrees C, and 1100 degrees C is shown in Table 1. The specific surface area after 6-hour heating was 24.2m²/g at 1100 degrees C. Moreover, as a result of the component analysis, the content rates of the zirconium in a multiple oxide, a cerium, and aluminum were a zirconium dioxide, the second cerium of oxidation, and aluminum-oxide conversion, and were 65.1 % of the weight, 30 % of the weight, and 4.9 % of the weight, respectively.

[0031] 16.67ml (water solution with a magnesium nitrate and 6 hydrate by Wako Pure Chem Industries, a% [of purity] of 99.9, and a magnesium-oxide conversion concentration of 150g [l.]) of magnesium nitrate water solutions was mixed with 81.05g of zirconium hydroxide used in the example 6 example 1, and cerium sol 150ml, and the mixture of ZrO₂:CeO₂:MgO=65:30:5 (weight ratio) was obtained. Furthermore, it added so that it might exist by the mol 6.1 times, and 1l. of total cerium mol mixture adjusted by desalted water so that it might become the oxide conversion concentration of 50g/l. was obtained for the nitric acid. Subsequently, it carried out like the example 1 and 137.79g precipitate was obtained. X diffraction measurement of the obtained precipitate was carried out on an example 1 and these conditions. Although the exact diameter of microcrystal was not able to be measured, the X-ray intensity which shows crystallinity was about 700cps. It carried out still like the example 1 and 50g of zirconium-cerium system magnesium content multiple oxides of specific-surface-area of 91.6m²/g was obtained. The specific surface area when heating the obtained multiple oxide for 6 hours each at 900 more degrees C, 1000 degrees C, and 1100 degrees C is shown in Table 1. The specific surface area after 6-hour heating was 25.3m²/g at 1100 degrees C. As a result of the component analysis, the content rates of the zirconium in a multiple oxide, a cerium, and magnesium were a zirconium dioxide, the second cerium of oxidation, and magnesium-oxide conversion, and were 65.1 % of the weight, 30 % of the weight, and 4.9 % of the weight, respectively.

[0032] 16.67ml of lanthanum nitrate water solutions was mixed with 81.05g of zirconium hydroxide used in the example 7 example 1, and cerium sol 150ml, and the mixture of ZrO₂:CeO₂:La₂O₃=65:30:5 (weight ratio) was obtained. Furthermore, it added so that it might exist by the mol 7 times, and 1l. of total cerium mol mixture adjusted by desalted water so that it might become the oxide conversion concentration of 50g/l. further was obtained for the nitric acid. Subsequently, it carried out like the example 1 and 138.04g precipitate was obtained. X diffraction measurement of the obtained precipitate was carried out on an example 1 and these conditions. Although the exact diameter of microcrystal was not able to be measured, the X-ray intensity which shows crystallinity was about 700cps. It carried out still like the example 1 and 50g of zirconium-cerium system lanthanum content multiple oxides of specific-surface-area of 108.1m²/g was obtained. The specific surface area when heating the obtained multiple oxide for 6 hours each at 900 more degrees C, 1000 degrees C, and 1100 degrees C is shown in Table 1. The specific surface area after 6-hour heating was 24.5m²/g at 1100 degrees C. As a result of the component analysis, the zirconium in a multiple oxide, the cerium, and the content rate of a lanthanum were a zirconium dioxide, the second cerium of oxidation, and lanthanum trioxide conversion, and were 65.1 % of the weight, 30 % of the weight, and 4.9 % of the weight, respectively.

[0033] 33.3ml of lanthanum nitrate water solutions was mixed with 81.05g of zirconium hydroxide used in the example 8 example 1, and cerium sol 83.3ml, and the mixture of ZrO₂:CeO₂:La₂O₃=65:25:10 (weight ratio) was obtained. Furthermore, it added so that it might exist by the mol 5.8 times, and 1l. of total cerium mol mixture adjusted by desalted water so that it might become the oxide conversion concentration of 50g/l. further was obtained for the nitric acid. Subsequently, it held for 6 hours, having put 1l. of obtained mixture into the pressurization reaction container (autoclave), and agitating under pressurization (2kg/cm²). Next, aqueous ammonia was added like the example 1, solid liquid separation of a product was performed, and 136.53g precipitate was obtained. X diffraction measurement of the obtained precipitate was carried out on an example 1 and these conditions. Although the exact diameter of microcrystal was not able to be measured, the X-ray intensity which shows crystallinity was about 700cps. Henceforth, it carried out like the example 1 and 50g of zirconium-cerium system lanthanum content multiple oxides of specific-surface-area of 102.6m²/g was obtained. The specific surface area when heating the obtained multiple oxide for 6 hours each at 900 more degrees C, 1000 degrees C, and 1100 degrees C is shown in Table 1. The specific surface area after 6-hour heating was 27m²/g at 1100 degrees C. As a result of the component analysis, the zirconium in a multiple oxide, the cerium, and the content rate of a lanthanum were a zirconium dioxide, the second cerium of oxidation, and lanthanum trioxide conversion, and were 65.1 % of the weight, 24.8 % of the weight, and 10.1 % of the weight, respectively.

[0034] 16.67ml of lanthanum nitrate water solutions was mixed with 130ml (triple-purpose metal industrial stock type firm make, purity of 99%, zirconium dioxide conversion concentration of 250g/l.) of example of comparison 1 zirconium-nitrate solutions, and cerium sol 150ml, and the mixture of ZrO₂:CeO₂:La₂O₃=65:30:5 (weight ratio) was obtained. Furthermore, 1l. of mixture adjusted by desalted water so that it might become the oxide conversion concentration of 50g/l. was obtained. Subsequently, it carried out like the example 1 and 141.21g precipitate was obtained. The obtained precipitate was gel. X diffraction measurement of the obtained precipitate was carried out on an example 1 and these conditions. An X diffraction image is shown in drawing 2. Although the exact diameter of microcrystal was not able to be measured, the X-ray intensity which shows crystallinity was about 500cps. Furthermore, it carried out like the example 1 and 50g of zirconium-cerium system lanthanum content multiple oxides of specific-surface-area of 97.7m²/g was obtained. The specific surface area when heating the obtained multiple oxide for 6 hours each at 900 more degrees C, 1000 degrees C, and 1100 degrees C is shown in Table 1 and drawing 5. The diameter of microcrystal for which it asked from the X diffraction image is shown in drawing 4. The specific surface area after 6-hour heating was 7.1m²/g at 1100 degrees C. As a result of the component analysis, the zirconium in a multiple oxide, the cerium, and the content rate of a lanthanum were a zirconium dioxide, cerium oxide, and lanthanum trioxide conversion, and were 65 % of the weight, 30.1 % of the weight, and 4.9 % of the weight, respectively.

[0035] 16.67ml of lanthanum nitrate water solutions was mixed with 81.05g of zirconium hydroxide used in the example of

comparison 2 example 1, and cerium sol 150ml, and the mixture of $\text{ZrO}_2\text{:CeO}_2\text{:La}_2\text{O}_3=65\text{:}30\text{:}5$ (weight ratio) was obtained. Furthermore, it added so that it might exist by the mol 11 times, and 1l. of total cerium mol mixture adjusted by desalted water so that it might become the oxide conversion concentration of 50g/l. further was obtained for the nitric acid. Subsequently, it carried out like the example 1 and 140.35g precipitate was obtained. The obtained precipitate was gel. X diffraction measurement of the obtained precipitate was carried out on an example 1 and these conditions. Although the exact diameter of microcrystal was not able to be measured, the X-ray intensity which shows crystallinity was about 500cps. It carried out still like the example 1 and 50g of zirconium-cerium system lanthanum content multiple oxides of specific-surface-area of 96m²/g was obtained. The specific surface area when heating the obtained multiple oxide for 6 hours each at 900 more degrees C, 1000 degrees C, and 1100 degrees C is shown in Table 1. The specific surface area after 6-hour heating was 7.6m²/g at 1100 degrees C. As a result of the component analysis, the zirconium in a multiple oxide, the cerium, and the content rate of a lanthanum were a zirconium dioxide, the second cerium of oxidation, and lanthanum trioxide conversion, and were 65.1 % of the weight, 30 % of the weight, and 4.9 % of the weight, respectively.

[0036] 16.67ml of lanthanum nitrate water solutions was mixed with 81.05g of zirconium hydroxide used in the example of comparison 3 example 1, and cerium sol 150ml, and the mixture of $\text{ZrO}_2\text{:CeO}_2\text{:La}_2\text{O}_3=65\text{:}30\text{:}5$ (weight ratio) was obtained. Furthermore, it added so that it might exist by the mol 4.5 times, and 1l. was obtained [the nitric acid] for the total cerium mol mixture adjusted by desalted water so that it might become the oxide conversion concentration of 50g/l. Subsequently, it carried out like the example 1 and 140.67g precipitate was obtained. The obtained precipitate was gel. X diffraction measurement of the obtained precipitate was carried out on an example 1 and these conditions. Although the exact diameter of microcrystal was not able to be measured, the X-ray intensity which shows crystallinity was about 500cps. It carried out still like the example 1 and 50g of zirconium-cerium system lanthanum content multiple oxides of specific-surface-area of 98.7m²/g was obtained. The specific surface area when heating the obtained multiple oxide for 6 hours each at 900 more degrees C, 1000 degrees C, and 1100 degrees C is shown in Table 1. The specific surface area after 6-hour heating was 3.3m²/g at 1100 degrees C. As a result of the component analysis, the zirconium in a multiple oxide, the cerium, and the content rate of a lanthanum were a zirconium dioxide, the second cerium of oxidation, and lanthanum trioxide conversion, and were 65 % of the weight, 30 % of the weight, and 5 % of the weight, respectively.

[0037] 16.67ml of lanthanum nitrate water solutions was mixed with zirconium sol (purity [of 99.9%], zirconium dioxide conversion concentration of 50g/l.) 650ml obtained by hydrolyzing example of comparison 4 zirconium oxychloride, and cerium sol 150ml, and the mixture of $\text{ZrO}_2\text{:CeO}_2\text{:La}_2\text{O}_3=65\text{:}30\text{:}5$ (weight ratio) was obtained. Furthermore, 1l. of mixture adjusted by desalted water so that it might become the oxide conversion concentration of 50g/l. was obtained. Subsequently, it carried out like the example 1 and 141.68g precipitate was obtained. X diffraction measurement of the obtained precipitate was carried out on an example 1 and these conditions. Although the exact diameter of microcrystal was not able to be measured, the X-ray intensity which shows crystallinity was about 500cps. It carried out still like the example 1 and 50g of zirconium-cerium system lanthanum content multiple oxides of specific-surface-area of 115.7m²/g was obtained. Chlorine was detected 0.18% of the weight. The specific surface area when heating the obtained multiple oxide for 6 hours each at 900 more degrees C, 1000 degrees C, and 1100 degrees C is shown in Table 1. The specific surface area after 6-hour heating was 6.9m²/g at 1100 degrees C. As a result of the component analysis, the zirconium in a multiple oxide, the cerium, and the content rate of a lanthanum were a zirconium dioxide, the second cerium of oxidation, and lanthanum trioxide conversion, and were 64.9 % of the weight, 30.2 % of the weight, and 4.9 % of the weight, respectively.

[0038]

[Table 1]

| 試料名 | 組成比(重量%) | | | | | | 比表面積(m ² /g) | | | |
|------|------------------|------------------|--------------------------------|--------------------------------|--------------------------------|-----|-------------------------|---------------|----------------|----------------|
| | ZrO ₂ | CeO ₂ | La ₂ O ₃ | Nd ₂ O ₃ | Al ₂ O ₃ | MgO | 500°C × 6hrs. | 900°C × 6hrs. | 1000°C × 6hrs. | 1100°C × 6hrs. |
| 実施例1 | 65.1 | 29.9 | 5 | — | — | — | 92.7 | 72.8 | 55.4 | 24.7 |
| 実施例2 | 74.9 | 20.2 | 4.9 | — | — | — | 115.7 | 70.9 | 51.7 | 22.4 |
| 実施例3 | 75 | 25 | — | — | — | — | 112.4 | 70.4 | 52 | 20.4 |
| 実施例4 | 65 | 30.1 | — | 4.9 | — | — | 91.3 | 70.9 | 54.9 | 23.8 |
| 実施例5 | 65.1 | 30 | — | — | 4.9 | — | 90.9 | 71.2 | 55 | 24.2 |
| 実施例6 | 65.1 | 30 | — | — | — | 4.9 | 91.6 | 72.6 | 56.1 | 25.3 |
| 実施例7 | 65.1 | 30 | 4.9 | — | — | — | 108.1 | 76.4 | 60.4 | 24.5 |
| 実施例8 | 65.1 | 24.8 | 10.1 | — | — | — | 102.6 | 81.7 | 63.1 | 27 |
| 比較例1 | 65 | 30.1 | 4.9 | — | — | — | 97.7 | 53.8 | 34 | 7.1 |
| 比較例2 | 65.1 | 30 | 4.9 | — | — | — | 96 | 51.4 | 32.9 | 7.6 |
| 比較例3 | 65 | 30 | 5 | — | — | — | 98.7 | 41.3 | 25.4 | 3.3 |
| 比較例4 | 64.9 | 30.2 | 4.9 | — | — | — | 115.7 | 70 | 39.1 | 6.9 |

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the graph which shows the X diffraction result of the precipitate before baking of an example 1.

[Drawing 2] It is the graph which shows the X diffraction result of the precipitate before baking of the example 1 of a comparison.

[Drawing 3] It is the graph which shows heating weight change (TG) of the precipitate of an example 1.

[Drawing 4] It is the graph which shows the heat-resistant comparison of the example 1 and the example 1 of a comparison which were expressed from burning temperature and the diameter of microcrystal.

[Drawing 5] It is the graph which shows the heat-resistant comparison of the example 1 and the example 1 of a comparison which were expressed from burning temperature and specific surface area.

[Translation done.]

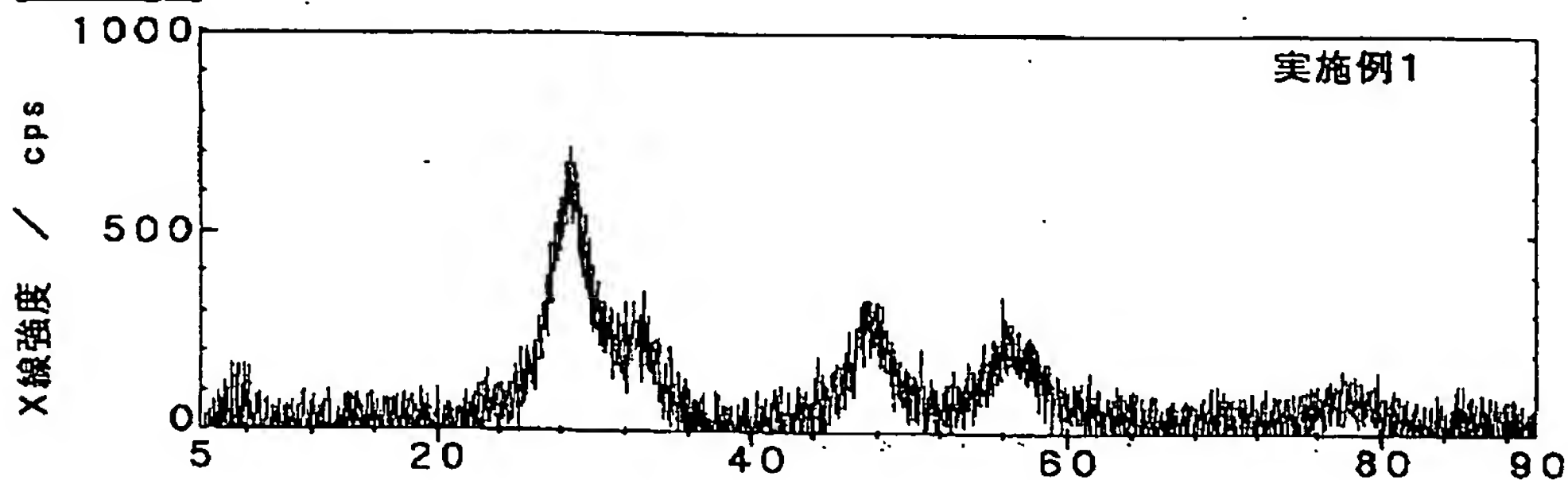
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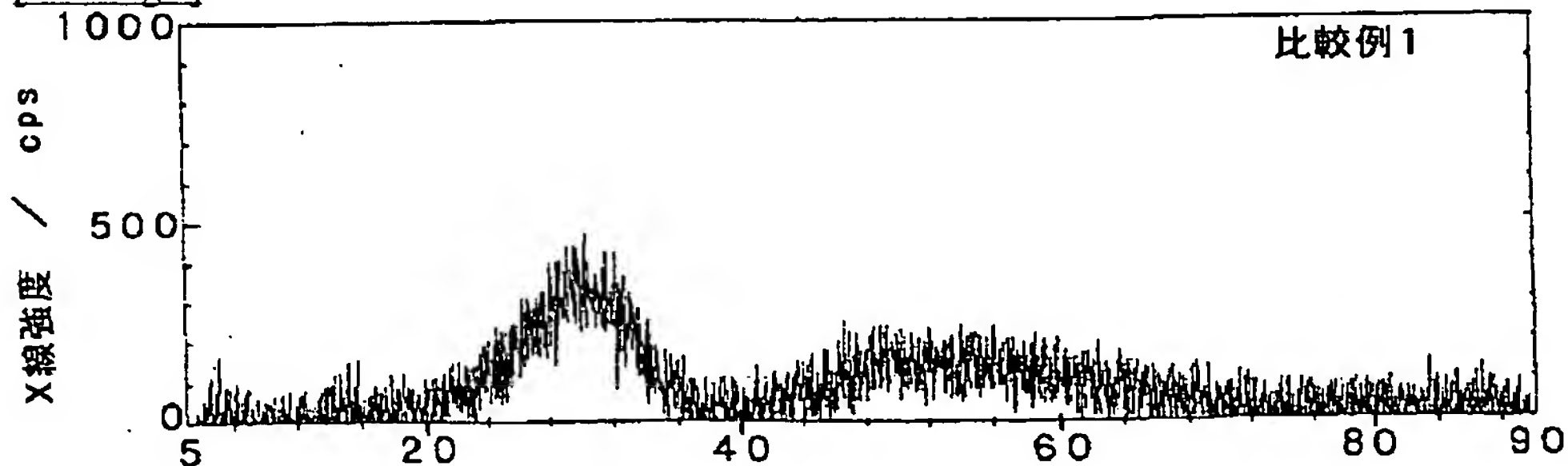
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DRAWINGS

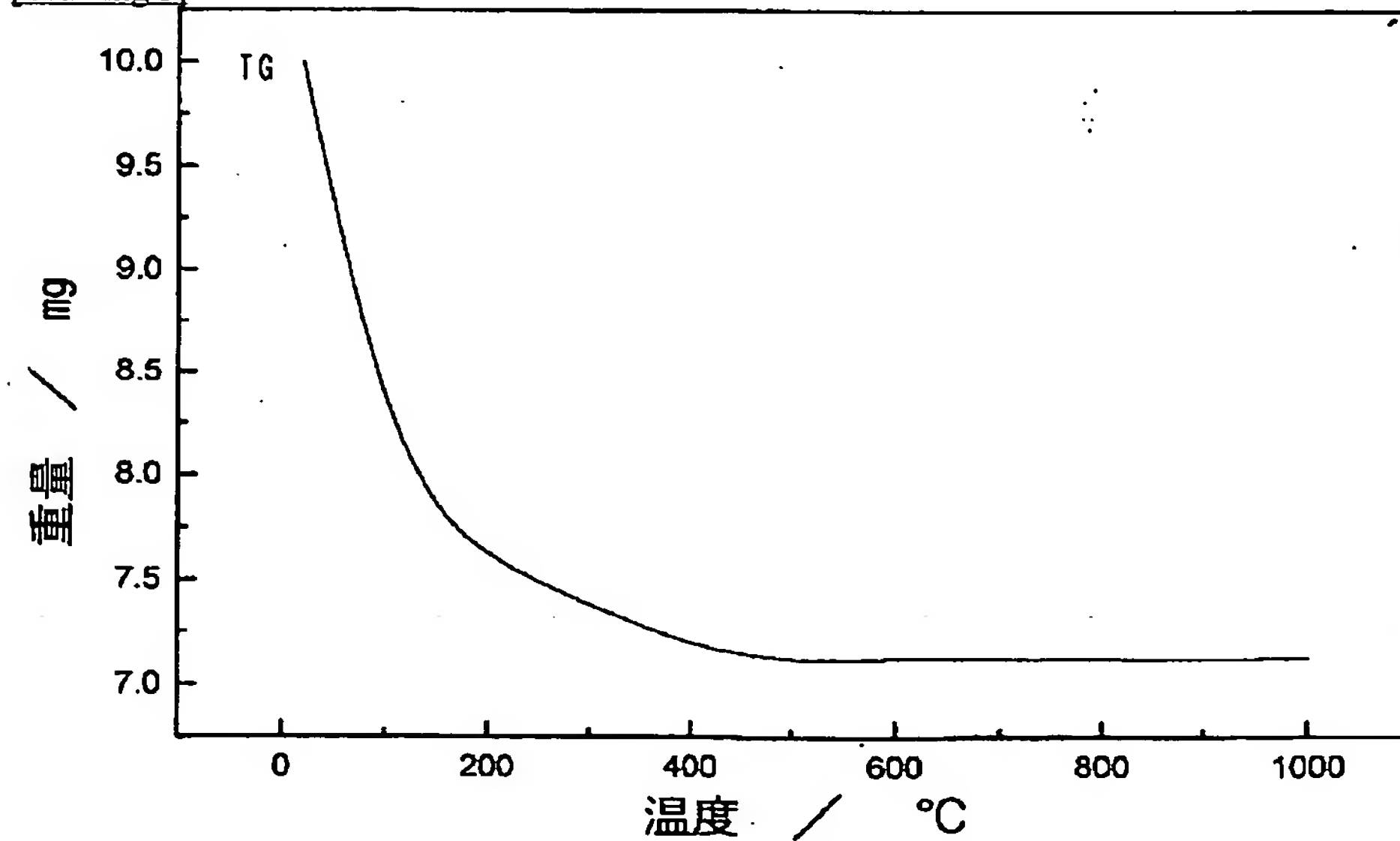
[Drawing 1]



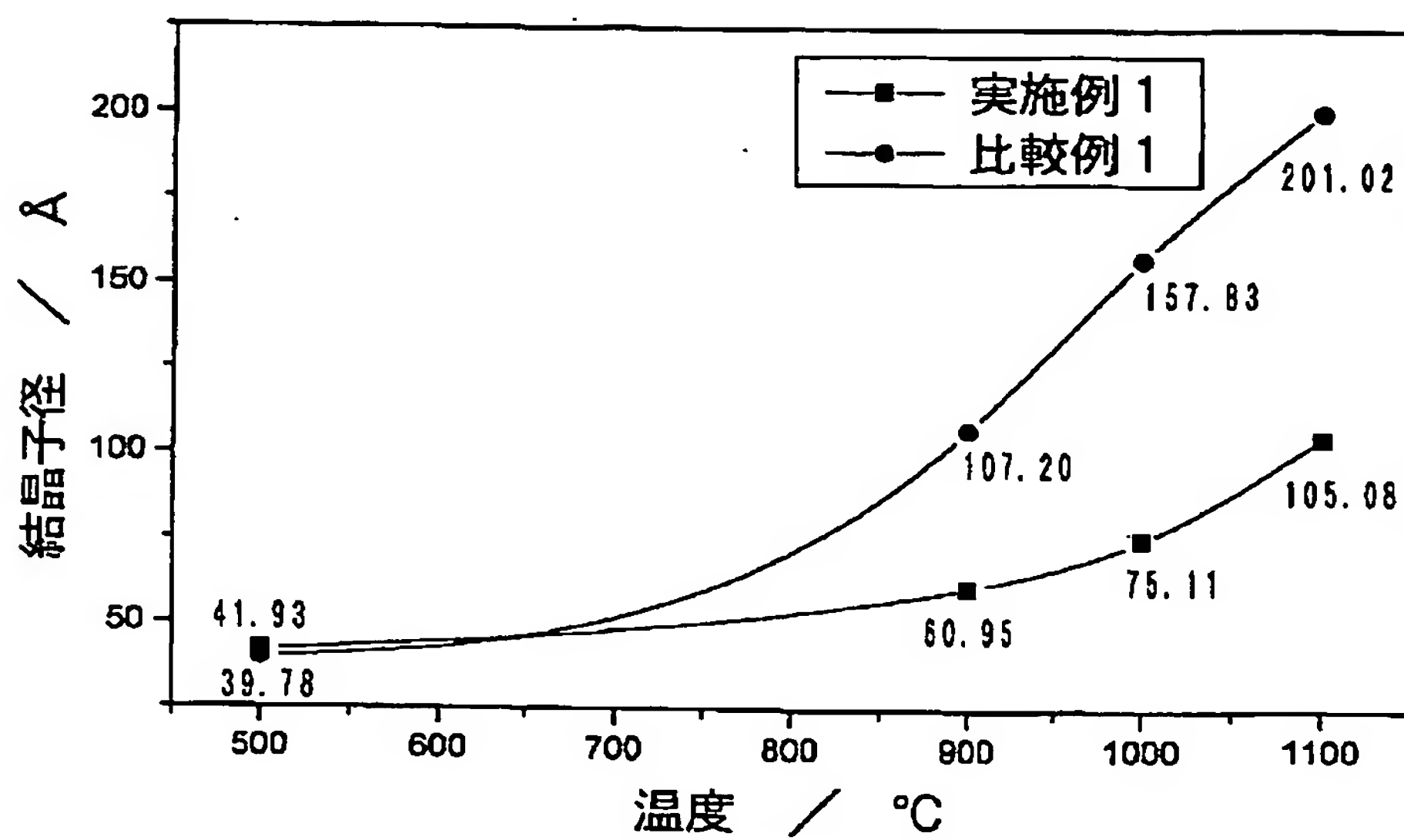
[Drawing 2]



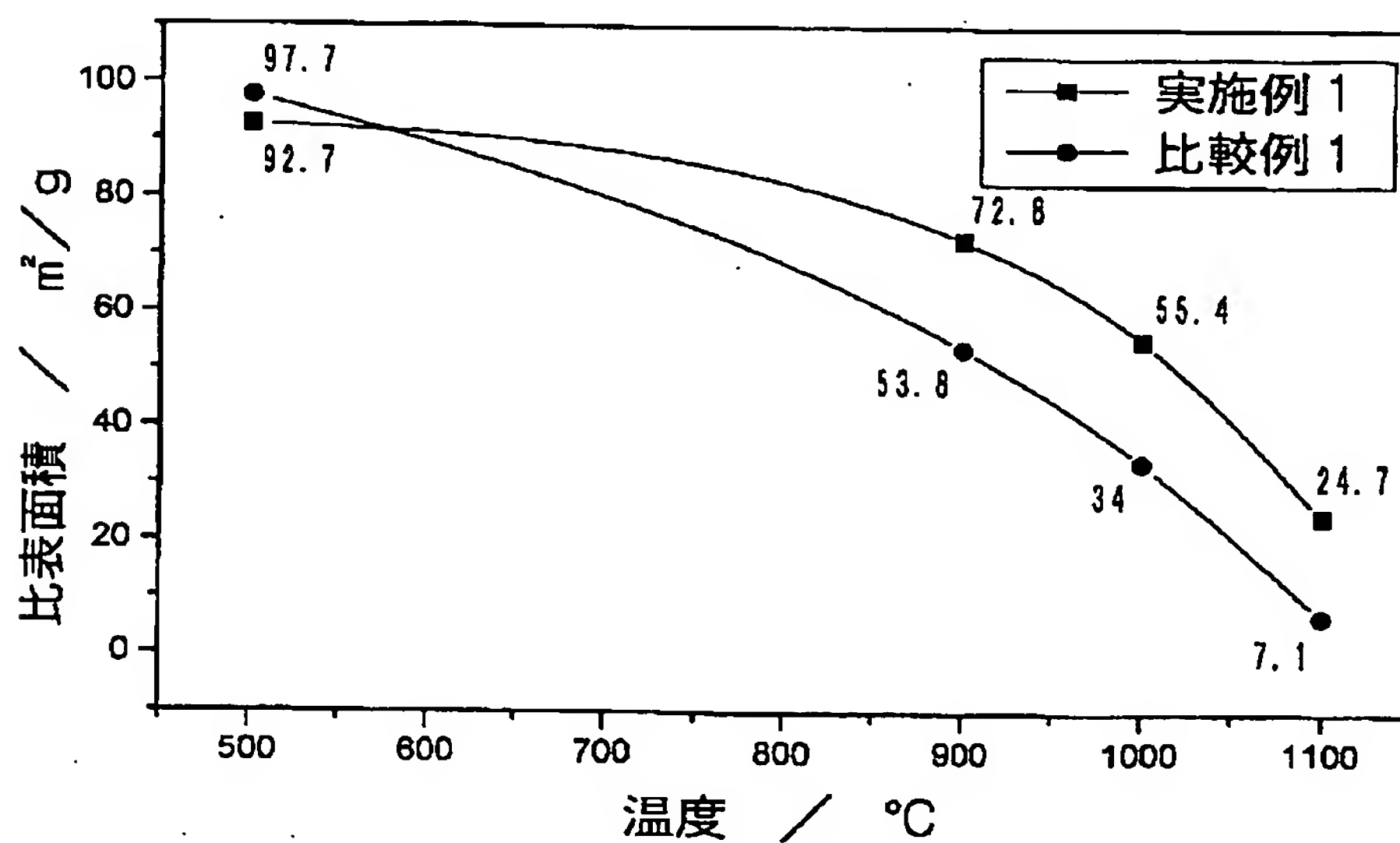
[Drawing 3]



[Drawing 4]



[Drawing 5]



[Translation done.]

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(54)【発明の名称】 ジルコニウム-セリウム系複合酸化物及びその製造方法

(57)【要約】

【課題】優れた耐熱性を有し、高温環境下で使用された場合においても高い比表面積を維持することが可能なジルコニウム-セリウム系複合酸化物及びこのような複合酸化物を再現性よく、且つ経済的に調製することが可能な製造方法を提供すること。

【解決手段】500～1000℃で焼成して得た複合酸化物であって、該複合酸化物が、ジルコニウム及びセリウムを含み、酸化ジルコニウム及び酸化第二セリウムに換算した前記ジルコニウム及びセリウムの配合比率が、重量比で51～95：49～5であり、前記500～1000℃で焼成した後の比表面積が少なくとも50m²/gを示し、かつ1100℃で6時間加熱後において少なくとも20m²/gの比表面積を維持しているジルコニウム-セリウム系複合酸化物及びその製造方法。

【特許請求の範囲】

【請求項1】 500～1000℃で焼成して得た複合酸化物であって、該複合酸化物が、ジルコニウム及びセリウムを含み、酸化ジルコニウム及び酸化第二セリウムに換算した前記ジルコニウム及びセリウムの配合比率が、重量比で51～95：49～5であり、前記500～1000℃で焼成した後の比表面積が少なくとも50 m²/gを示し、かつ1100℃で6時間加熱後において少なくとも20 m²/gの比表面積を維持していることを特徴とするジルコニウム－セリウム系複合酸化物。

【請求項2】 前記複合酸化物が、さらにイットリウム、スカンジウム、ランタン、プラセオジウム、ネオジウム、サマリウム、ユーロピウム、ガドリニウム、マグネシウム、カルシウム、バリウム、アルミニウム、チタン及びハフニウムからなる群より選択される1種又は2種以上を、酸化物換算しての合計量で0.1～20重量%含有することを特徴とする請求項1記載のジルコニウム－セリウム系複合酸化物。

【請求項3】 平均粒径0.5～50 μmの水酸化ジルコニウムと、コロイド粒子の平均粒径3～100 nmのセリウムゾルとを含む混合物を、該混合物中のセリウムモル数に対して5～10倍モルの硝酸存在下に、加熱反応させ、次いで、塩基を加えて更に反応させ、得られた生成物を500～1000℃で焼成し、粉砕することを特徴とする請求項1又は2に記載のジルコニウム－セリウム系複合酸化物の製造方法。

【請求項4】 前記混合物が、イットリウム、スカンジウム、ランタン、プラセオジウム、ネオジウム、サマリウム、ユーロピウム、ガドリニウム、マグネシウム、カルシウム、バリウム、アルミニウム、チタン及びハフニウムの塩類からなる群より選択される1種又は2種以上を含む請求項3記載のジルコニウム－セリウム系複合酸化物の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、触媒分野、機能性セラミックス分野、燃料電池用固体電解質分野等に利用可能であり、特に自動車の排ガス浄化用触媒における助触媒材料として好適に利用可能な優れた耐熱性を有するジルコニウム－セリウム系複合酸化物及びその製造法に関する。

【0002】

【従来の技術】自動車などの排ガス浄化用触媒は、例えばアルミナ、コーゼライト等の触媒担持体に触媒金属である白金、パラジウム、ロジウム等とこれらの触媒作用を高めるための助触媒が担持されて構成される。この助触媒材料としての酸化セリウム系材料は、酸化雰囲気下で酸素を吸収し、還元雰囲気下でその酸素を放出するという酸化セリウムの特性、いわゆる酸素吸収・放出能により排ガス中の有害成分である炭化水素、一酸化炭素

及び窒素酸化物等を優れた効率で浄化するために大量に使用されている。また、酸化ジルコニウムは、前記酸化セリウムの特性を高めることから、助触媒材料としては、ジルコニウム－セリウム系複合酸化物が主流となり使用比率が増加してきている。

【0003】この系の助触媒材料を機能させるときに最も重要なことは高温を維持することであり、エンジン始動時のように排ガスの温度が低いときは浄化効率が悪。近年、自動車メーカーはエンジンと触媒装置の距離を近付け、排気直後の高温排ガスを触媒装置に導入することでこの問題に対処しようとしている。

【0004】しかし、この場合触媒材料の耐熱性に関して新たな問題が生じた。触媒による排ガス処理の効率は一般に触媒の活性相と排ガスの接触面積に比例することから、使用される助触媒材料は充分に比表面積の大きいものでなければならない。しかし、現状のジルコニウム－セリウム系複合酸化物の粒子は、高温長時間の使用環境では粒成長により比表面積が低下することから、耐熱性に関して十分とは言えず、安定して高比表面積の維持される助触媒材料が強く求められている。

【0005】従来の耐熱性に優れたジルコニウム－セリウム系複合酸化物の製造方法に関しては、例えば特開平6-279027号公報及び特公平8-16015号公報に、ジルコニウムゾルとセリウムゾルとを混合し塩基を加える方法、又は噴霧乾燥を用いる方法が提案されている。そして、得られた混合酸化物の耐熱性については、1000℃仮焼後の比表面積が15 m²/gであることが記載されている。特開平5-193948号公報には、平均粒径0.2 μm以下の水和ジルコニアゾルと、Ce、Y、Ca、Mgなどの化合物との混合物を焼成する混合酸化物の製造方法が提案されており、得られた混合酸化物の耐熱性は、1050℃仮焼後の比表面積が12 m²/gであることが記載されている。特開平5-116945号公報には、平均粒径0.05～0.3 μm及び結晶子径4 nm以下の水和ジルコニアゾルと、Ce、Y、Ca、Mgなどの化合物との混合物を焼成する混合酸化物の製造方法が提案されており、得られた混合酸化物の耐熱性は、850℃焼成後の比表面積が15 m²/gであることが記載されている。また、ジルコニウム酸化物の製造方法として、特開平5-155622号公報には、ジルコニウム塩水溶液に、2価以上の金属の水酸化物・水和酸化物・酸化物などを混合し、加水分解させる方法が提案されており、得られた混合酸化物の耐熱性は、1000℃焼成後の比表面積が8 m²/gであることが記載されている。

【0006】以上のいずれの方法も目的とする酸化物を製造する操作時間が長いという問題がある。例えば、ジルコニアゾルの入手が必要な方法では、ジルコニウム塩水溶液の加水分解時間が100時間を越えるなどの生産性に問題がある。

【0007】また、単に高比表面積を得る方法としては、酸化物の結晶子径、すなわち結晶の成長度合いを抑制すればよく、例えば、特開平6-279027号公報及び特公平8-16015号公報に記載されるジルコニアゾル（5～500nmの微細なジルコニア・コロイド粒子）を用いる製造方法が最適である。しかし、酸化物の状態における結晶・粒子径が微細であるが故に熱エネルギーに対して非常に敏感であり、これら既知の製造方法によって得られた酸化物は、900℃以上の高温域での焼結において、著しく比表面積が小さくなり耐熱性が悪いという問題がある。即ち、高温使用される助触媒材料には適していない。更に、従来提案されている多くの製造方法では、原料に起因する触媒にとって有害である塩素、硫黄等の不純物混入が避けられないという問題もある。

【0008】

【発明が解決しようとする課題】従って本発明の目的は、特に排ガス浄化用触媒に適した助触媒材料として優れた耐熱性を有し、高温環境下で使用された場合においても高い比表面積を維持することが可能なジルコニウム-セリウム系複合酸化物及びその製造方法を提供することにある。本発明の別の目的は、優れた耐熱性を有するジルコニウム-セリウム系複合酸化物を、再現性よく、且つ経済的に調製することが可能な製造方法を提供することにある。本発明の他の目的は、優れた耐熱性を有すると共に触媒にとって有害な塩素、硫黄等の不純物の混入のないジルコニウム-セリウム系複合酸化物の製造方法を提供することにある。

【0009】

【課題を解決するための手段】本発明者は、従来技術によるジルコニウム-セリウム系複合酸化物が、大きな比表面積を持つ場合でも高温に加熱すると急激に比表面積が低下する原因に関し、ジルコニウム原料の影響について詳細な研究を行った。その結果、従来酸化ジルコニウムと酸化セリウムとの固溶度の高い複合酸化物を得る方法として知られている、ジルコニウムゾル或いはジルコニウム塩の水溶液と、セリウムゾル或いはセリウム塩水溶液とを混合し、塩基を添加して生成させた複合酸化物前駆体は、微結晶性であるためか熱エネルギーに対して極めて敏感であり、焼成により固溶度の高い単相の結晶相をもつジルコニウム-セリウム系複合酸化物を生成するが高温域での焼結による比表面積の低下が著しく、高比表面積を維持できないことを確認した。そこで、前駆体の段階で結晶度を高める試みを試行錯誤したところ、このような高比表面積の複合酸化物用途におけるジルコニウム原料として、これまで取り上げられなかった水酸化ジルコニウム粒子の利用とその粒度の影響について検討した結果、この粒子を母体として、セリウム成分、或いは更に他の添加成分を複合させた前駆体を得るための反応方法を開発し、本発明を完成するに至った。

【0010】すなわち、本発明によれば、500～1000℃で焼成して得た複合酸化物であって、該複合酸化物が、ジルコニウム及びセリウムを含み、酸化ジルコニウム及び酸化第二セリウムに換算した前記ジルコニウム及びセリウムの配合比率が、重量比で51～95：49～5であり、必要により、さらにイットリウム、スカンジウム、ランタン、プラセオジウム、ネオジウム、サマリウム、ユーロピウム、ガドリニウム、マグネシウム、カルシウム、バリウム、アルミニウム、チタン及びハフニウムからなる群より選択される1種又は2種以上を、酸化物換算しての合計量で0.1～20重量%含有し、前記500～1000℃で焼成した後の比表面積が少なくとも50m²/gを示し、かつ1100℃で6時間加熱後において少なくとも20m²/gの比表面積を維持していることを特徴とするジルコニウム-セリウム系複合酸化物が提供される。また、本発明によれば、平均粒径0.5～50μmの水酸化ジルコニウムと、コロイド粒子の平均粒径3～100nmのセリウムゾルとを、また必要に応じてイットリウム、スカンジウム、ランタン、プラセオジウム、ネオジウム、サマリウム、ユーロピウム、ガドリニウム、マグネシウム、カルシウム、バリウム、アルミニウム、チタン及びハフニウムの塩類からなる群より選択される1種又は2種以上を含む混合物を、該混合物中のセリウムモル数に対して5～10倍モルの硝酸存在下に、加熱反応させ、次いで、塩基を加えて更に反応させ、得られた生成物を500～1000℃で焼成し、粉碎することを特徴とする前記ジルコニウム-セリウム系複合酸化物の製造方法が提供される。

【0011】

【発明の実施の形態】以下本発明の更に詳細に説明する。本発明のジルコニウム-セリウム系複合酸化物において、複合酸化物とは、酸化ジルコニウムと酸化セリウムとが単に混合物の状態でなく、部分的又は実質的に複合酸化物乃至固溶体を形成しているものを言う。この複合酸化物を助触媒材料として使用した場合に酸素吸収・放出能を示すのは、酸化セリウム成分であるが、酸化ジルコニウム成分はこの酸化セリウムの耐熱性を高め、広い温度範囲で酸素吸収・放出能を発揮させる作用を有する。

【0012】本発明の複合酸化物において、含有されるジルコニウム及びセリウムの配合比率は、酸化ジルコニウム（ZrO₂）及び酸化第二セリウム（CeO₂）に換算した重量比で51～95：49～5、好ましくは55～85：45～15、更に好ましくは60～80：40～20である。酸化ジルコニウムの配合比率が51未満では、優れた耐熱性が十分に得られず、また95を越えると酸化セリウム成分による酸素吸収・放出能が不足する。複合酸化物中のジルコニウム及びセリウムの合計含有割合は、酸化ジルコニウム及び酸化第二セリウム換算で80重量%以上が好ましい。

【0013】本発明の複合酸化物は、500～1000℃で焼成して得られ、この温度範囲で焼成した後の比表面積は、少なくとも50m²/gを示し、通常、焼成温度が高いほど比表面積が低くなる。例えば500℃で6時間の焼成であれば90m²/g以上、900℃で6時間の焼成であれば70m²/g以上、1000℃で6時間の焼成であれば50m²/g以上の高い比表面積を示す。このような焼成温度における高水準の比表面積を有する材料はジルコニウム-セリウム系複合酸化物としては、従来知られていない。そして、本発明の複合酸化物は、1100℃で6時間加熱後において少なくとも20m²/gの比表面積を維持する性能を有する。一般に酸化物粉末を加熱する場合、組成及びその粉末の製造履歴に依存する特定の温度領域以上において焼結及び粒成長が顕著になり、急激な比表面積の低下が生じる。ジルコニウム-セリウム系複合酸化物においては、大略1000℃以上でこの減少が顕著であることが知られ、現行の排ガス浄化用触媒装置も通常は約900℃以下で稼働するように設計されている。本発明では今後求められる1000℃前後の高温で使用可能な助触媒材料等にも使用可能である複合酸化物の性能を示すために、得られた複合酸化物の耐熱性の評価温度としては使用される温度の上限とみなされる1100℃を基準とし、1100℃で6時間加熱後に維持されている比表面積の値を複合酸化物の性能指標とした。なお、本発明において比表面積とは、粉体の比表面積測定法として最も標準的な窒素ガス吸着によるBET法に基づいて測定された値である。

【0014】本発明の複合酸化物は、ジルコニウム及びセリウムの他に、更にイットリウム、スカンジウム、ランタン、プラセオジウム、ネオジウム、サマリウム、ユーロピウム、ガドリニウム、マグネシウム、カルシウム、バリウム、アルミニウム、チタン及びハフニウムからなる群より選択される1種又は2種以上を酸化物換算して合計量で0.1～20重量%の範囲で含有していても良い。このような特定の金属を更に含有させることにより、一層優れた耐熱性を付与することが可能である。この際、0.1重量%未満では耐熱性改善に効果が認められず、また20重量%を越えるとセリウムの含有量が相対的に低下し、助触媒等に使用した場合に要求される酸素吸収・放出能が不足するので好ましくない。

【0015】本発明の製造方法は、前記複合酸化物を再現性よく、且つ経済的に調製することができる。この製造方法では、まず、特定のジルコニウム原料と、特定のセリウム原料とを含む混合物を、特定量の硝酸存在下に加熱反応させる。

【0016】前記特定のジルコニウム原料は、平均粒径0.5～50μm、好ましくは1～30μm、更に好ましくは5～25μmの水酸化ジルコニウムである。平均粒径が0.5μm未満の場合は本発明の目的とする耐熱性に優れた高比表面積の複合酸化物が得られず、50μ

mを越える場合は複合酸化物の比表面積が低下する。該水酸化ジルコニウムとは、(1)水酸化ジルコニウムZr(OH)₄・nH₂O、(2)オキシ水酸化ジルコニウムZrO(OH)₂・nH₂O、(3)水和ジルコニアZrO₂・nH₂Oの総称であって、単独若しくは混合物として用いることができる。前記水酸化ジルコニウムは、通常粉体の状態で市販品から入手できるが、例えば硝酸ジルコニウム、塩化ジルコニウム、硝酸ジルコニル等のジルコニウム塩水溶液にアンモニア水、アンモニアガス、水酸化ナトリウム、水酸化カリウム等の塩基を加える等の公知の方法で得ることができる。中でも、硝酸ジルコニル-アンモニア系の製法は、塩素、硫黄等の有害不純物を含まない点で有利である。なお、平均粒径の測定はレーザー回折法に基づくリーズ&ノースラップ社製粒度分析計(MKII型)により行った。

【0017】前記特定のセリウム原料は、コロイド粒子の平均粒径3～100nm、好ましくは5～80nm、さらに好ましくは10～50nmのセリウムゾルである。該セリウムゾルとは、一般に理解されるように、コロイド粒子サイズの酸化セリウム、水和酸化セリウム、水酸化セリウムのいずれかまたは複数の形の固体微粒子(コロイド粒子)が水性媒体中に分散した状態のものをいう。コロイド粒子の平均粒径が3nm未満の場合には工業的に製造が困難であり、100nmを越える場合は、後工程において酸化ジルコニウムとの複合化が進行し難い。なお、コロイド粒子径の測定は動的光散乱測定法に基づく大塚電子社製ダイナミック光散乱光度計(DLS-7000型)により行った。前記セリウムゾルの製造法は特に限定されるものではなく、例えば硝酸第二セリウム水溶液を加水分解させる公知の方法などによって得られ、また市販品として、酸化セリウム換算で100～200g/リットル程度の濃度のものが利用できる。市販のセリウムゾルは、ゾル状態を安定に保持するために、硝酸酸性或いは酢酸酸性されているものがあるがいずれでも使用可能である。但し、セリウムゾルを製造するときの原料に起因する塩素、硫黄等の不純物の残留の極力少ないものの使用が望ましい。

【0018】前記混合物において、前記水酸化ジルコニウム及び前記セリウムゾルの混合割合は、所望のジルコニウム-セリウム系複合酸化物の組成比に対応する理論比となるように適宜設定することができ、例えば、ジルコニウム及びセリウムを酸化ジルコニウム及び酸化第二セリウムに換算した混合割合が、重量比で51～95:49～5となるように混合するのが好ましい。混合物の調製は、前記水酸化ジルコニウム及び前記セリウムゾルを秤量し適量の水と共に混合し、スラリー状の混合物とするのが好ましい。混合物中の前記水酸化ジルコニウム及び前記セリウムゾルの濃度は、酸化物換算の合計量で10～200g/リットル、特に20～150g/リットルが望ましい。前記混合物には、必要に応じて、更に

イットリウム、スカンジウム、ランタン、プラセオジウム、ネオジウム、サマリウム、ユーロピウム、ガドリニウム、マグネシウム、カルシウム、バリウム、アルミニウム、チタン及びハフニウムの塩類からなる群より選択される1種又は2種以上を添加することができる。塩類としては、硝酸塩、塩化物、硫酸塩、その他水溶性塩類の中から選び得るが、水溶性塩以外でも次工程において硝酸酸性下で加熱した時に溶解してイオン化する化合物であれば使用可能である。特に有害不純物が得られる複合酸化物中に残存しない硝酸塩が好ましい。これら塩類の混合量は、得られる複合酸化物中に、酸化物換算しての合計量が0.1～20重量%となるような理論比で秤量し混合するのが好ましい。これらジルコニウム、セリウム以外の混合成分は、得られる複合酸化物中に固溶乃至酸化物として微細分散し、高温での複合酸化物の結晶成長を妨げる作用を有する。

【0019】前記混合物の加熱反応は、攪拌下行うのが好ましく、この際、混合物中のセリウムモル数に対して、5～10倍モル、好ましくは5.5～8倍モル、さらに好ましくは5.8～7倍モルの硝酸を存在させる必要がある。前述のセリウムゾルとして硝酸酸性で安定化されたタイプのものをを用いた場合は、その硝酸量をも含めてトータルで硝酸が上記モル数となるように調製すればよく、酢酸酸性で安定化されたタイプのものでは上記モル数となるように硝酸を添加すればよい。このような特定量の硝酸を存在させることにより、水酸化ジルコニウム、セリウムゾルの粒子それぞれの結晶が溶出及び析出を繰り返し、ジルコニウム、セリウムの複合化を行いつつ結晶成長を進行させることができる。硝酸が5倍モル未満では、結晶成長は不十分となり得られる複合酸化物に優れた耐熱性を付与できない。一方、10倍モルを越えると水酸化ジルコニウム粒子が溶解し、イオン状態のジルコニウムが増すため、後述する塩基との反応において微細沈殿が生じて本発明の意図する十分に成長した前駆体を得られず、耐熱性に優れた複合酸化物が得られない。

【0020】前記硝酸存在下の加熱反応は、反応温度60～150℃、好ましくは80～140℃で、反応時間1～36時間の範囲で行うことができる。好ましくは常圧又は加圧下で行うことができる。加圧下で実施する場合には、例えば、オートクレーブ等の加圧容器を用い、1.5～10kg/cm²程度の加圧下で行うことにより反応時間を短縮することが可能である。

【0021】本発明の製造方法では、次いで塩基を加えて更に反応させる。この反応にあたっては、例えば、前記硝酸の存在下反応させた混合物を、好ましくは60℃以下、特に好ましくは50℃以下に冷却した後、塩基を加えて攪拌等して反応を進行させることができる。塩基としては、水酸化ナトリウム、水酸化カリウム、アンモニア水、アンモニアガス又はこれらの混合物等を挙げる

ことができるが、好ましくはアンモニア水である。塩基の添加は、塩基を適度な濃度の水溶液とし、前記冷却された混合物に攪拌しながら加える方法、アンモニアガスの場合は攪拌しながら容器内に吹き込む方法等により行うことができる。加える塩基の量の限度は混合物のpHの変化を追うことによって容易に判定され、pHが10を越えれば十分であり、反応が完了する。この反応により、混合物中に存在した固形物及び金属イオンは実質的に全て複合化され、結晶成長の進んだ生成物を沈澱させることができる。図1及び図2は後述する本発明の実施例（実施例1）と比較例1におけるこの段階の生成物を同一条件（実施例の項で記述）でX線回折測定した結果であり、本発明による生成物が結晶性の高いものであることが分かる。この生成物が耐熱性に優れた所望の複合酸化物を得るために好適な前駆体となる。この前駆体は、例えばヌッチェ法、遠心分離法、フィルタープレス法等で分離することができる。また、必要程度に沈殿物の水洗を付加することもできる。更に、次の焼成工程の効率を高めるために、得られた沈殿物を適度に乾燥する工程を付加してもよい。

【0022】本発明の製造方法では、前記得られた生成物を特定温度で焼成し、粉碎することにより所望の複合酸化物を得ることができる。焼成温度は500～1000℃の間の任意の温度を選択できる。下限温度を500℃としたのは次の理由による。図3において、生成物の加熱重量変化を熱天秤（リガク電機社製造TG-DTA-812H型使用）を用いて測定した結果から、重量減少は500℃で完了していることが分かる。すなわち、焼成温度が500℃未満ではジルコニウム-セリウム系複合酸化物が未完成であり、水酸基、酸基、塩基等が残留しているため、高温下で使用する際、それらが放出されるので採用できない。図4は、500℃以上の温度領域において、本発明（後述の実施例1）と比較例1による複合酸化物について、焼成温度（各6時間）に対する結晶子径の変化を比較して調べたものである。図5はそれらに対応する比表面積の変化である。両図より、本発明による複合酸化物が高温域で焼成した場合でも、結晶子が粗大化しにくく（焼結性が低く）、従って高い比表面積を維持していることが分かる。所望の複合酸化物とするための焼成温度は、要求される、または保証する比表面積及び嵩密度の値から任意に選び得るが、比表面積を重視する助触媒材料としての実用的観点から上限は1000℃以下に限定する。好ましくは500～800℃、更に好ましくは500～600℃である。焼成時間は温度との兼ね合いで適宜設定してよく、好ましくは1～10時間である。本発明による複合酸化物は、500～1000℃の範囲であればその焼成条件如何によらず、優れた耐熱性を有し、1100℃6時間加熱においてなお20m²/g以上の高い比表面積を有している。

【0023】前記粉碎は、焼成された複合酸化物を、一

一般的に用いられる粉碎機、例えばハンマーミル等を用いて実施でき、十分所望の粒度の粉末を得ることができる。これは、得られた複合酸化物の焼結性が小さいため、粉碎性が良好でありことに基づく。

【0024】

【発明の効果】本発明の複合酸化物は、ジルコニウムとセリウムとの複合酸化物を主成分とし、高い比表面積を有し、特に1100℃6時間の加熱後においても少なくとも20m²/gの比表面積を維持する優れた耐熱性を有するので、従来のジルコニウム-セリウム系複合酸化物に代えて特に排ガス浄化用触媒の助触媒等として利用でき、従来の限界以上の高温域での使用が可能であり、高効率の排ガス浄化用触媒の分野において極めて有用である。また本発明の製造法では、前記高比表面積と高耐熱性を有する複合酸化物を、再現性よく、しかも経済的に得ることができる。

【0025】

【実施例】以下、実施例及び比較例により更に詳細に説明するが、本発明はこれらに限定されるものではない。

【0026】実施例1

水酸化ジルコニウム（三徳金属工業株式会社製、純度99.9%、酸化ジルコニウム換算含有量40.1重量%、平均粒径18.56μm）81.05gと、セリウムゾル（ローヌ・プーラン社製、セリウムイオン含有量5重量%以下、酸化セリウム換算濃度100g/リットル）150mlと、硝酸ランタン水溶液（阿南化成株式会社製、純度99.9%、酸化ランタン換算濃度150g/リットル）16.67mlとを混合し、 $ZrO_2 : CeO_2 : La_2O_3 = 65 : 30 : 5$ （重量比）の混合物を得た。得られた混合物に、更に硝酸（和光純薬工業株式会社製、純度60～61%）を総セリウムモルの6倍モル分存在するように添加し、更に酸化物換算濃度が50g/リットルとなるように脱塩水で調整した混合物を1リットル得た。次いで得られた混合物1リットルを水蒸気冷却管（コンデンサー）を備えた容器に移し100℃で12時間、攪拌下で加熱した。20℃まで徐冷した後、アンモニア水（和光純薬工業株式会社製、NH₃含有量25～28重量%）を攪拌下で添加し、pHを10以上に調整した。得られた生成物をヌッチェで固液分離を行い、沈殿物を139.23g得た。得られた沈殿物をリガク社製「RINT1100型」X線回折装置でCuKα線、管電圧40kV、管電流40mAにより測定した。X線回折像を図1に示す。正確な結晶子径は測定不能であったが、結晶性を示すX線強度は約700cpsであった。得られた沈殿物を500℃で6時間焼成し、比表面積92.7m²/gのジルコニウム-セリウム系ランタン含有複合酸化物50gを得た。得られた複合酸化物を更に900℃、1000℃、及び1100℃にて各6時間加熱したときの比表面積を表1及び図5に示す。また、X線回折像から求めた結晶子径を図4に示

す。1100℃で6時間加熱後の比表面積は24.7m²/gであった。組成分析の結果、複合酸化物中のジルコニウム、セリウム及びランタンの含有割合は、酸化ジルコニウム、酸化第二セリウム及び酸化ランタン換算で、それぞれ65.1重量%、29.9重量%、及び5重量%であった。

【0027】実施例2

実施例1で用いた水酸化ジルコニウム93.52gとセリウムゾル100ml及び硝酸ランタン水溶液16.67mlとを混合し、 $ZrO_2 : CeO_2 : La_2O_3 = 75 : 20 : 5$ （重量比）の混合物を得た。得られた混合物に、更に硝酸を総セリウムモルの6.2倍モル分存在するように添加し、更に酸化物換算濃度が50g/リットルとなるように脱塩水で調整した混合物を1リットル得た。次いで、実施例1と同様に攪拌・加熱し、アンモニア水を添加し、生成物の固液分離を行って、142gの沈殿物を得た。得られた沈殿物を実施例1と同条件でX線回折測定した。正確な結晶子径は測定不能であったが、結晶性を示すX線強度は約700cpsであった。更に実施例1と同様に焼成を行って、比表面積115.7m²/gのジルコニウム-セリウム系ランタン含有複合酸化物50gを得た。得られた複合酸化物を更に900℃、1000℃、及び1100℃にて各6時間加熱したときの比表面積を表1に示す。1100℃で6時間加熱後の非表面積は22.4m²/gであった。組成分析の結果、複合酸化物中のジルコニウム、セリウム及びランタンの含有割合は、酸化ジルコニウム、酸化第二セリウム及び酸化ランタン換算で、それぞれ74.9重量%、20.2重量%及び4.9重量%であった。

【0028】実施例3

実施例1で用いた水酸化ジルコニウム93.52gとセリウムゾル125mlとを混合し、 $ZrO_2 : CeO_2 = 75 : 25$ （重量比）の混合物を得た。得られた混合物に、更に硝酸を総セリウムモルの5.5倍モル分存在するように添加し、更に酸化物換算濃度50g/リットルとなるように脱塩水で調整した混合物を1リットル得た。次いで、実施例1と同様に行って141.62gの沈殿物を得た。得られた沈殿物を実施例1と同条件でX線回折測定した。正確な結晶子径は測定不可能であったが、結晶性を示すX線強度は約700cpsであった。更に実施例1と同様に行って比表面積112.4m²/gのジルコニウム-セリウム複合酸化物50gを得た。得られた複合酸化物をさらに900℃、1000℃、及び1100℃にて各6時間加熱したときの比表面積を表1に示す。1100℃で6時間加熱後の非表面積は20.4m²/gであった。また、組成分析の結果、複合酸化物中のジルコニウム、セリウムの含有割合は、酸化ジルコニウム、酸化第二セリウム換算で、それぞれ75重量%、25重量%であった。

【0029】実施例4

実施例1で用いた水酸化ジルコニウム81.05gとセリウムゾル150mlと、硝酸ネオジム水溶液（阿南化成株式会社製、純度99.9%、酸化ネオジム換算濃度150g/リットル）16.67mlとを混合し、 $ZrO_2 : CeO_2 : Nd_2O_3 = 65 : 30 : 5$ （重量比）の混合物を得た。更に硝酸を総セリウムモルの6.5倍モル分存在するように添加し、更に酸化物換算濃度50g/リットルとなるように脱塩水で調整した混合物を1リットル得た。次いで、実施例1と同様に行って138.24gの沈殿物を得た。得られた沈殿物を実施例1と同条件でX線回折測定した。正確な結晶子径は測定不可能であったが、結晶性を示すX線強度は約700cpsであった。さらに実施例1と同様に行って比表面積91.3m²/gのジルコニウム-セリウム系ネオジム含有複合酸化物50gを得た。得られた複合酸化物をさらに900℃、1000℃、及び1100℃にて各6時間加熱したときの比表面積を表1に示す。1100℃で6時間加熱後の比表面積は23.8m²/gであった。組成分析の結果、複合酸化物中のジルコニウム、セリウム及びネオジムの含有割合は、酸化ジルコニウム、酸化第二セリウム及び酸化ネオジム換算で、それぞれ65重量%、30.1重量%及び4.9重量%であった。

【0030】実施例5

実施例1で用いた水酸化ジルコニウム81.05gと、セリウムゾル150mlと、硝酸アルミニウム水溶液（和光純薬工業株式会社製の硝酸アルミニウム・9水和物、純度99.9%、酸化アルミニウム換算濃度150g/lの水溶液）16.67mlとを混合し、 $ZrO_2 : CeO_2 : Al_2O_3 = 65 : 30 : 5$ （重量比）の混合物を得た。更に硝酸を総セリウムモルの6.1倍モル分存在するように添加し、更に酸化物換算濃度50g/リットルとなるように脱塩水で調整した混合物を1リットル得た。次いで、実施例1と同様に行って137.94gの沈殿物を得た。得られた沈殿物を実施例1と同条件でX線回折測定した。正確な結晶子径は測定不可能であったが、結晶性を示すX線強度は約700cpsであった。さらに実施例1と同様に行って比表面積90.9m²/gのジルコニウム-セリウム系アルミニウム含有複合酸化物50gを得た。得られた複合酸化物をさらに900℃、1000℃、及び1100℃にて各6時間加熱したときの比表面積を表1に示す。1100℃で6時間加熱後の比表面積は24.2m²/gであった。また、組成分析の結果、複合酸化物中のジルコニウム、セリウム及びアルミニウムの含有割合は、酸化ジルコニウム、酸化第二セリウム及び酸化アルミニウム換算で、それぞれ65.1重量%、30重量%及び4.9重量%であった。

【0031】実施例6

実施例1で用いた水酸化ジルコニウム81.05gと、セリウムゾル150mlと、硝酸マグネシウム水溶液

（和光純薬工業株式会社製の硝酸マグネシウム・6水和物、純度99.9%、酸化マグネシウム換算濃度150g/リットルの水溶液）16.67mlとを混合し、 $ZrO_2 : CeO_2 : MgO = 65 : 30 : 5$ （重量比）の混合物を得た。更に硝酸を総セリウムモルの6.1倍モル分存在するように添加し、酸化物換算濃度50g/リットルとなるように脱塩水で調整した混合物を1リットル得た。次いで、実施例1と同様に行って137.79gの沈殿物を得た。得られた沈殿物を実施例1と同条件でX線回折測定した。正確な結晶子径は測定不可能であったが、結晶性を示すX線強度は約700cpsであった。さらに実施例1と同様に行って比表面積91.6m²/gのジルコニウム-セリウム系マグネシウム含有複合酸化物50gを得た。得られた複合酸化物をさらに900℃、1000℃、及び1100℃にて各6時間加熱したときの比表面積を表1に示す。1100℃で6時間加熱後の比表面積は25.3m²/gであった。組成分析の結果、複合酸化物中のジルコニウム、セリウム及びマグネシウムの含有割合は、酸化ジルコニウム、酸化第二セリウム及び酸化マグネシウム換算で、それぞれ65.1重量%、30重量%及び4.9重量%であった。

【0032】実施例7

実施例1で用いた水酸化ジルコニウム81.05gと、セリウムゾル150mlと、硝酸ランタン水溶液16.67mlとを混合し、 $ZrO_2 : CeO_2 : La_2O_3 = 65 : 30 : 5$ （重量比）の混合物を得た。更に硝酸を総セリウムモルの7倍モル分存在するように添加し、更に酸化物換算濃度50g/リットルとなるように脱塩水で調整した混合物を1リットル得た。次いで、実施例1と同様に行って138.04gの沈殿物を得た。得られた沈殿物を実施例1と同条件でX線回折測定した。正確な結晶子径は測定不可能であったが、結晶性を示すX線強度は約700cpsであった。さらに実施例1と同様に行って比表面積108.1m²/gのジルコニウム-セリウム系ランタン含有複合酸化物50gを得た。得られた複合酸化物をさらに900℃、1000℃、及び1100℃にて各6時間加熱したときの比表面積を表1に示す。1100℃で6時間加熱後の比表面積は24.5m²/gであった。組成分析の結果、複合酸化物中のジルコニウム、セリウム及びランタンの含有割合は、酸化ジルコニウム、酸化第二セリウム及び酸化ランタン換算で、それぞれ65.1重量%、30重量%及び4.9重量%であった。

【0033】実施例8

実施例1で用いた水酸化ジルコニウム81.05gと、セリウムゾル83.3mlと、硝酸ランタン水溶液33.3mlとを混合し、 $ZrO_2 : CeO_2 : La_2O_3 = 65 : 25 : 10$ （重量比）の混合物を得た。更に硝酸を総セリウムモルの5.8倍モル分存在するように添加し、更に酸化物換算濃度50g/リットルとなるように

脱塩水で調整した混合物を1リットル得た。次いで、得られた混合物1リットルを加圧反応容器（オートクレーブ）に入れて加圧下（ 2 kg/cm^2 ）で攪拌しながら6時間保持した。次に実施例1と同様にアンモニア水を添加し、生成物の固液分離を行って136.53gの沈殿物を得た。得られた沈殿物を実施例1と同条件でX線回折測定した。正確な結晶子径は測定不可能であったが、結晶性を示すX線強度は約700cpsであった。以後、実施例1と同様に行って比表面積 $102.6\text{ m}^2/\text{g}$ のジルコニウム-セリウム系ランタン含有複合酸化物50gを得た。得られた複合酸化物を更に900℃、1000℃、及び1100℃にて各6時間加熱したときの比表面積を表1に示す。1100℃で6時間加熱後の比表面積は $27\text{ m}^2/\text{g}$ であった。組成分析の結果、複合酸化物中のジルコニウム、セリウム及びランタンの含有割合は、酸化ジルコニウム、酸化第二セリウム及び酸化ランタン換算で、それぞれ65.1重量%、24.8重量%及び10.1重量%であった。

【0034】比較例1

硝酸ジルコニル溶液（三徳金属工業株式会社製、純度99%、酸化ジルコニウム換算濃度 250 g/l ）130mlと、セリウムゾル150mlと、硝酸ランタン水溶液16.67mlとを混合し、 $\text{ZrO}_2:\text{CeO}_2:\text{La}_2\text{O}_3=65:30:5$ （重量比）の混合物を得た。更に酸化物換算濃度 50 g/l となるように脱塩水で調整した混合物を1リットル得た。次いで、実施例1と同様に行って141.21gの沈殿物を得た。得られた沈殿物はゲル状であった。得られた沈殿物を実施例1と同条件でX線回折測定した。X線回折像を図2に示す。正確な結晶子径は測定不可能であったが、結晶性を示すX線強度は約500cpsであった。更に実施例1と同様に行って比表面積 $97.7\text{ m}^2/\text{g}$ のジルコニウム-セリウム系ランタン含有複合酸化物50gを得た。得られた複合酸化物を更に900℃、1000℃、及び1100℃にて各6時間加熱したときの比表面積を表1及び図5に示す。X線回折像から求めた結晶子径を図4に示す。1100℃で6時間加熱後の比表面積は $7.1\text{ m}^2/\text{g}$ であった。組成分析の結果、複合酸化物中のジルコニウム、セリウム及びランタンの含有割合は、酸化ジルコニウム、酸化セリウム、及び酸化ランタン換算で、それぞれ65重量%、30.1重量%及び4.9重量%であった。

【0035】比較例2

実施例1で用いた水酸化ジルコニウム81.05gと、セリウムゾル150mlと、硝酸ランタン水溶液16.67mlとを混合し、 $\text{ZrO}_2:\text{CeO}_2:\text{La}_2\text{O}_3=65:30:5$ （重量比）の混合物を得た。更に硝酸を総セリウムモルの11倍モル分存在するように添加し、更に酸化物換算濃度 50 g/l となるように脱塩水で調整した混合物を1リットル得た。次いで、実施例1

と同様に行って140.35gの沈殿物を得た。得られた沈殿物はゲル状であった。得られた沈殿物を実施例1と同条件でX線回折測定した。正確な結晶子径は測定不可能であったが、結晶性を示すX線強度は約500cpsであった。さらに実施例1と同様に行って比表面積 $96\text{ m}^2/\text{g}$ のジルコニウム-セリウム系ランタン含有複合酸化物50gを得た。得られた複合酸化物をさらに900℃、1000℃、及び1100℃にて各6時間加熱したときの比表面積を表1に示す。1100℃で6時間加熱後の比表面積は $7.6\text{ m}^2/\text{g}$ であった。組成分析の結果、複合酸化物中のジルコニウム、セリウム及びランタンの含有割合は、酸化ジルコニウム、酸化第二セリウム及び酸化ランタン換算で、それぞれ65.1重量%、30重量%及び4.9重量%であった。

【0036】比較例3

実施例1で用いた水酸化ジルコニウム81.05gと、セリウムゾル150mlと、硝酸ランタン水溶液16.67mlとを混合し、 $\text{ZrO}_2:\text{CeO}_2:\text{La}_2\text{O}_3=65:30:5$ （重量比）の混合物を得た。更に硝酸を総セリウムモルの4.5倍モル分存在するように添加し、酸化物換算濃度 50 g/l となるように脱塩水で調整した混合物を1リットル得た。次いで、実施例1と同様に行って140.67gの沈殿物を得た。得られた沈殿物はゲル状であった。得られた沈殿物を実施例1と同条件でX線回折測定した。正確な結晶子径は測定不可能であったが、結晶性を示すX線強度は約500cpsであった。さらに実施例1と同様に行って比表面積 $98.7\text{ m}^2/\text{g}$ のジルコニウム-セリウム系ランタン含有複合酸化物50gを得た。得られた複合酸化物をさらに900℃、1000℃、及び1100℃にて各6時間加熱したときの比表面積を表1に示す。1100℃で6時間加熱後の比表面積は $3.3\text{ m}^2/\text{g}$ であった。組成分析の結果、複合酸化物中のジルコニウム、セリウム及びランタンの含有割合は、酸化ジルコニウム、酸化第二セリウム及び酸化ランタン換算で、それぞれ65重量%、30重量%及び5重量%であった。

【0037】比較例4

オキシ塩化ジルコニウムを加水分解して得られたジルコニウムゾル（純度99.9%、酸化ジルコニウム換算濃度 50 g/l ）650mlと、セリウムゾル150mlと、硝酸ランタン水溶液16.67mlとを混合し、 $\text{ZrO}_2:\text{CeO}_2:\text{La}_2\text{O}_3=65:30:5$ （重量比）の混合物を得た。更に酸化物換算濃度 50 g/l となるように脱塩水で調整した混合物を1リットル得た。次いで、実施例1と同様に行って141.68gの沈殿物を得た。得られた沈殿物を実施例1と同条件でX線回折測定した。正確な結晶子径は測定不可能であったが、結晶性を示すX線強度は約500cpsであった。さらに実施例1と同様に行って比表面積 $115.7\text{ m}^2/\text{g}$ のジルコニウム-セリウム系ランタン含有複合

酸化物50gを得た。塩素が0.18重量%検出された。得られた複合酸化物をさらに900℃、1000℃、及び1100℃にて各6時間加熱したときの比表面積を表1に示す。1100℃で6時間加熱後の比表面積は6.9m²/gであった。組成分析の結果、複合酸化物中のジルコニウム、セリウム及びランタンの含有割合

は、酸化ジルコニウム、酸化第二セリウム及び酸化ランタン換算で、それぞれ64.9重量%、30.2重量%及び4.9重量%であった。

【0038】

【表1】

| 試料名 | 組成比(重量%) | | | | | | 比表面積(m ² /g) | | | |
|------|------------------|------------------|--------------------------------|--------------------------------|--------------------------------|-----|-------------------------|------------|-------------|-------------|
| | ZrO ₂ | CeO ₂ | La ₂ O ₃ | Nd ₂ O ₃ | Al ₂ O ₃ | MgO | 500℃×6hrs. | 900℃×6hrs. | 1000℃×6hrs. | 1100℃×6hrs. |
| 実施例1 | 65.1 | 29.9 | 5 | — | — | — | 92.7 | 72.8 | 55.4 | 24.7 |
| 実施例2 | 74.9 | 20.2 | 4.9 | — | — | — | 115.7 | 70.9 | 51.7 | 22.4 |
| 実施例3 | 75 | 25 | — | — | — | — | 112.4 | 70.4 | 52 | 20.4 |
| 実施例4 | 65 | 30.1 | — | 4.9 | — | — | 91.3 | 70.9 | 54.9 | 23.8 |
| 実施例5 | 65.1 | 30 | — | — | 4.9 | — | 90.9 | 71.2 | 55 | 24.2 |
| 実施例6 | 65.1 | 30 | — | — | — | 4.9 | 91.6 | 72.6 | 56.1 | 25.3 |
| 実施例7 | 65.1 | 30 | 4.9 | — | — | — | 108.1 | 76.4 | 60.4 | 24.5 |
| 実施例8 | 65.1 | 24.8 | 10.1 | — | — | — | 102.6 | 81.7 | 63.1 | 27 |
| 比較例1 | 65 | 30.1 | 4.9 | — | — | — | 97.7 | 53.8 | 34 | 7.1 |
| 比較例2 | 65.1 | 30 | 4.9 | — | — | — | 96 | 51.4 | 32.9 | 7.6 |
| 比較例3 | 65 | 30 | 5 | — | — | — | 98.7 | 41.3 | 25.4 | 3.3 |
| 比較例4 | 64.9 | 30.2 | 4.9 | — | — | — | 115.7 | 70 | 39.1 | 6.9 |

【図面の簡単な説明】

【図1】実施例1の焼成前沈殿物のX線回折結果を示すグラフである。

【図2】比較例1の焼成前沈殿物のX線回折結果を示すグラフである。

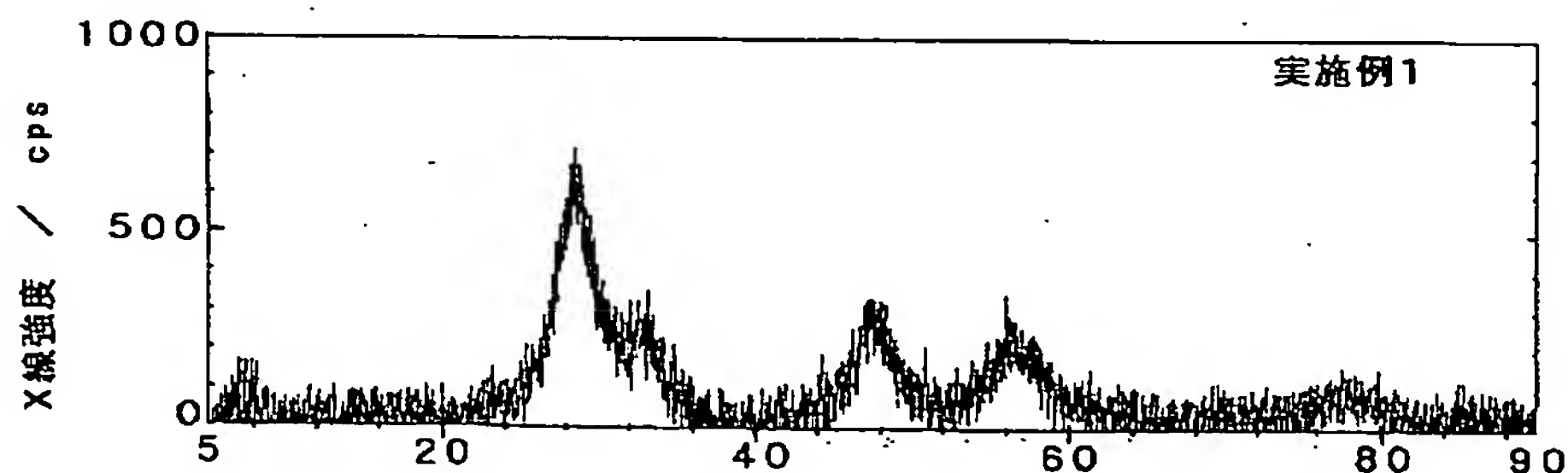
【図3】実施例1の沈殿物の加熱重量変化(TG)を示

すグラフである。

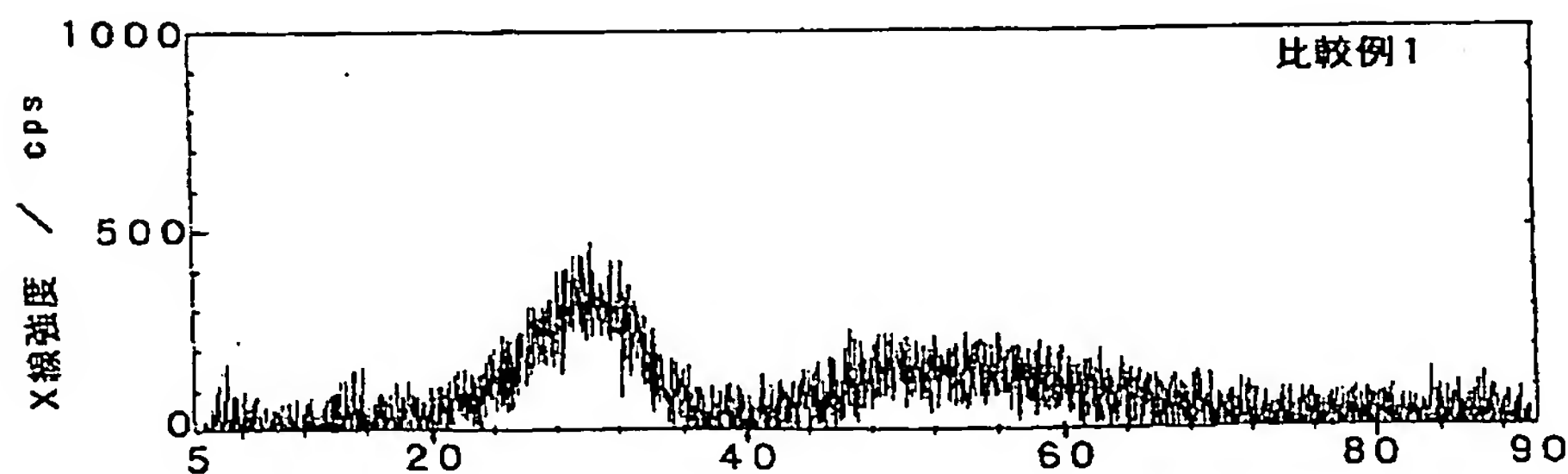
【図4】焼成温度と結晶子径から表した、実施例1と比較例1の耐熱性の比較を示すグラフである。

【図5】焼成温度と比表面積から表した、実施例1と比較例1の耐熱性の比較を示すグラフである。

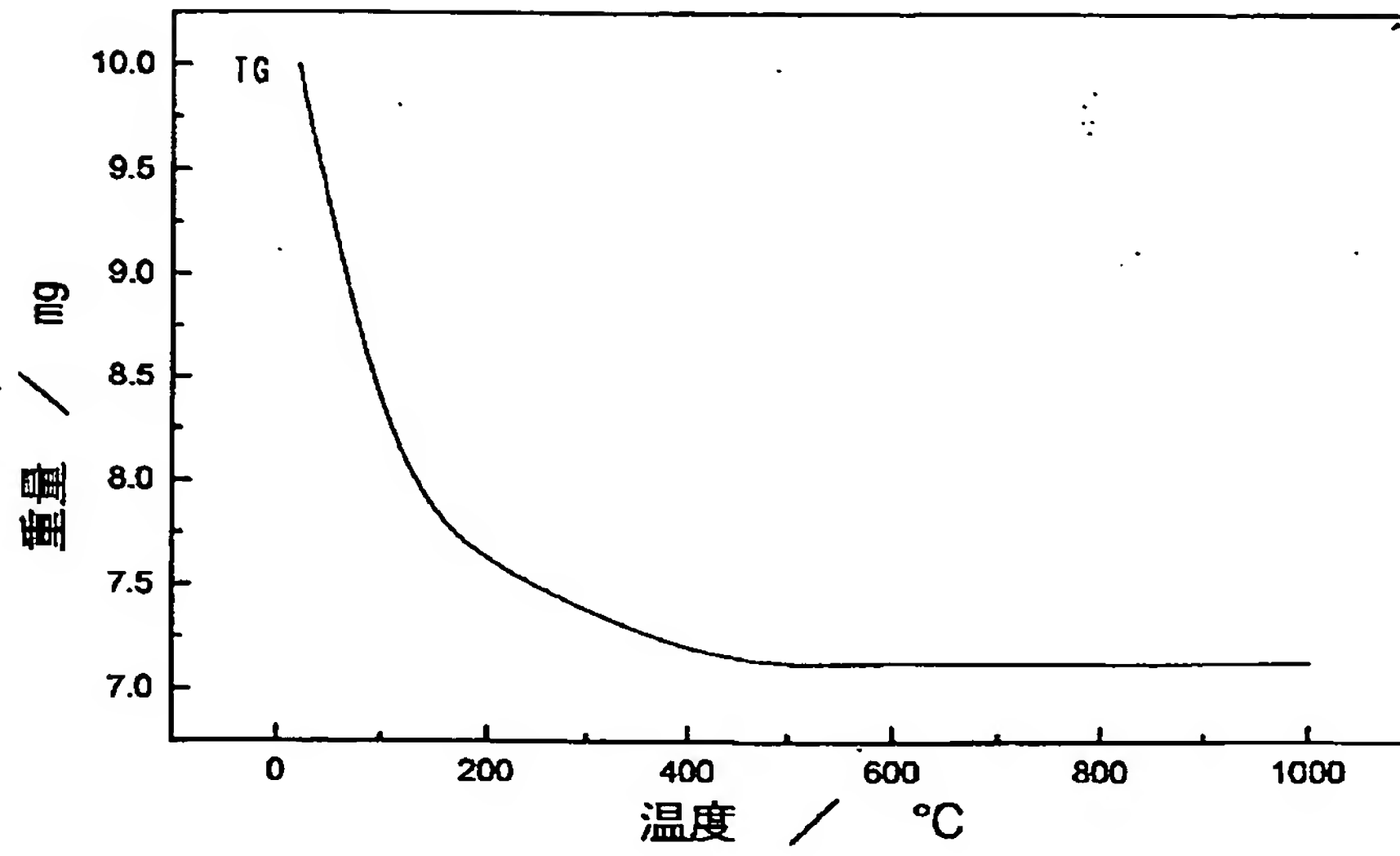
【図1】



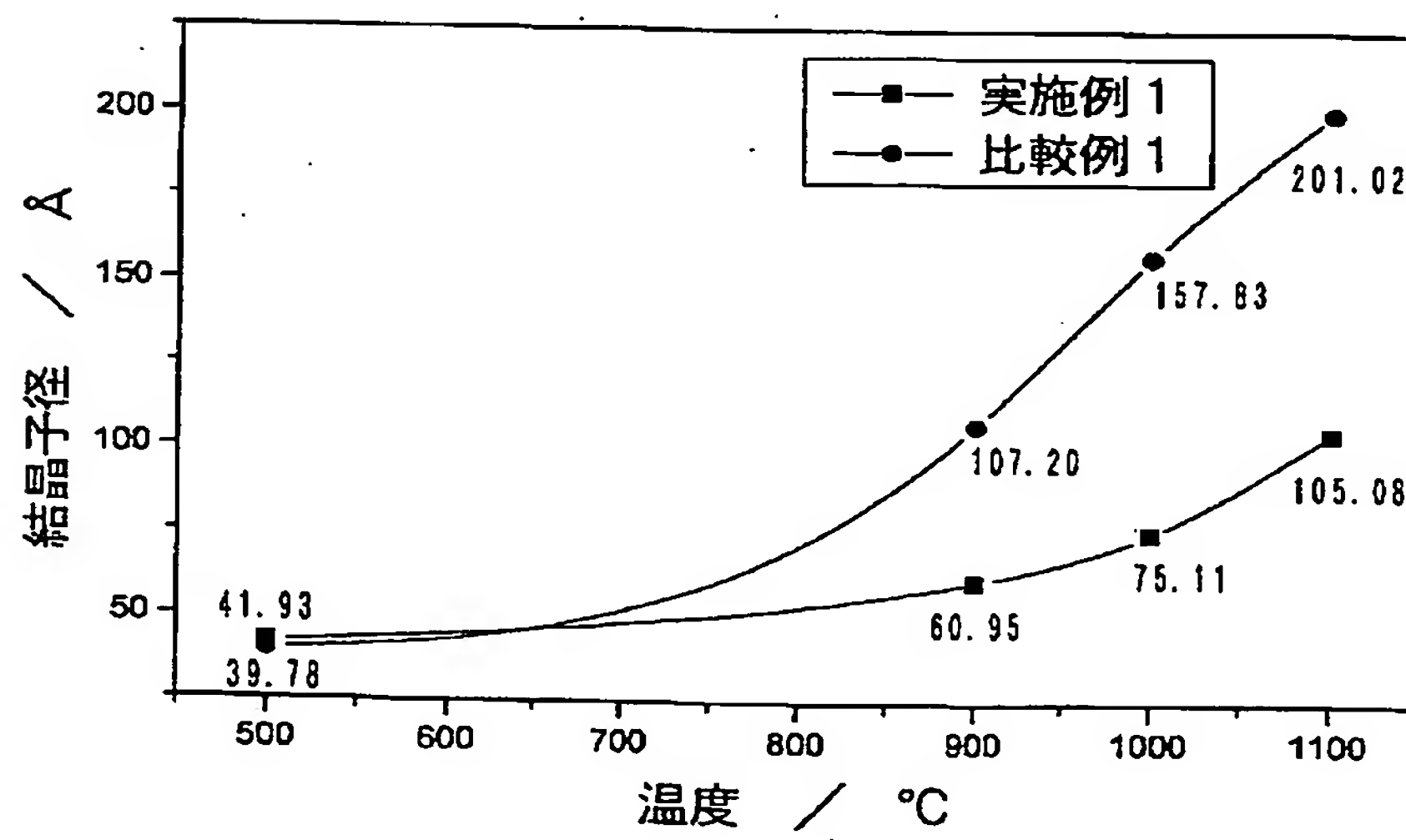
【図2】



【図3】



【図4】



【図5】

